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STEAM REFORMING OF METHYL FUEL - PHASE I

FINAL REPORT

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STEAM REFORMING OF METHYL FUEL - PHASE I

FINAL REPORT

JUNE 30, 1977

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ABSTRACT

An experimental study was made on the effects of gasoline contamination of methanol relative to steam reforming of the mixture.

At the conventional steam reforming temperature of $359-400^{\circ}F$ soot was produced with a 90/10 mixture of methanol and gasoline (by weight). A parametric study was conducted to evaluate the effects of higher temperature and higher steam to carbon ratio with four different catalysts.

Soot-free operation was obtained with Girdler catalyst T-2107 at an operating temperature of 750^CF at a steam to (total) carbon ratio of 3.8. Essentially all the gasoline is converted into light gaseous hydrocarbons, primarily methane. A trace of light-yellow oil droplets could be detected in the cooled product gas condensate.

A 100 hour test showed no deterioration of the T-2107 catalyst activity under the above conditions.

1.0 PROJECT PROGRAM

1.1 Introduction

Methanol is an excellent fuel for fuel cells. It is more convenient to store than hydrogen. It can be readily steam reformed to hydrogen and CO₂ at relatively low temperatures and low steam/carbon ratios. The U.S. Army Material Development and Readiness Command has developed a methanol steam reforming unit to supply hydrogen to a portable fuel cell power plant of 3KW capacity. During handling and storage of methanol in the field, it could become contaminated with gasoline or diesel fuel. It is difficult to steam reform such contaminated methanol as steam reforming of the hydrocarbons from gasoline or diesel fuel requires breaking of carbon-carbon bonds. This normally requires temperatures of 1200°F or above, while the steam reforming of methanol can take place at 350-400°F.

A contract was granted to JPL to investigate the effect of such hydrocarbon contamination, and to find a potential solution to this problem. The overall objective was to screen a number of promising catalysts over a range of temperatures to find an optimum set of operating conditions for gasification of gasoline contaminated methanol. If such a condition was found, a long duration life time test (100 hours) would be carried out to prove the technical feasibility of the concept.

In previous work at IGT the steam reforming of methanol contaminated with small amounts of ethanol, propanol and butanol was studied. This mixture simulated impure methanol that could be produced from coal processing, and which is normally called methyl fuel. This work showed that carbon deposition would take place on the catalyst at the normal operating temperature of 350-400°F.

It appeared that gasoline would be a worse contaminant to handle than ${\rm C_2-C_4}$ alcohols. It was decided to study gasoline contamination first, and that any solution for gasoline contamination should take care of the ${\rm C_2-C_4}$ alcohols also.

1.2 Program Goals

The objective of this program was to successfully steam reform methanol contaminated with gasoline. The following goals were to be obtained:

- 1.2.1 Determine the minimum reactor bed temperature, steam to carbon ratio, and space velocity for methanol/gasoline mixtures with several promising catalysts in order to produce a gasified product that can be utilized in a phosphoric acid fuel cell. This implies that the CO concentration in the product gas should be less than one percent.
- 1.2.2 Determine the effect of the contaminants on catalyst activity, specifically any reduction in activity by carbon deposition.
- 1.2.3 Determine the minimum reactor bed temperature and steam to carbon ratio to prevent soot formation.
- 1.2.4 If successful, demonstrate process feasibility by a continuous 100 hour test conducted at the optimum operating conditions and with the best catalyst.

2.0 TEST DESCRIPTION

2.1 Technical Background

The basic reactions occurring in steam reforming of methanol are

$$cH_3OH + H_2O \implies cO_2 + 3H_2$$

$$co_2 + H_2 \longrightarrow co + H_2o$$

However, at a temperature of 400° F and at atmospheric pressure, the predicted thermodynamic equilbria is as follows:

$$\text{CH}_3\text{OH} + 1.5 \text{ H}_2\text{O} \longrightarrow .26 \text{ CO} + 0.97 \text{ CO}_2 + 0.526 \text{ H}_2\text{O} + 2.97 \text{ H}_2$$

This corresponds to a CO concentration of 0.6 volume percent (wet).

The steam reforming reaction of unleaded gasoline ($\mathrm{CH}_{1.94}$) may be described as

$$CH_{1.94} + H_2O \longrightarrow CO + 1.97 H_2$$

This reaction normally takes place at $1200^{\circ}\mathrm{F}$ or above over a nickel catalyst. It is not possible to steam reform gasoline by itself at lower temperatures. Thus the big unknown factor at the beginning of this work was what temperature would be required to steam reform mixtures of methanol and gasoline.

These reactions are endothermic i.e., external heat must be supplied through a heat exchanger surface. The carbon monoxide that is formed can react with more steam, if available, according to the shift reaction:

$$co + H_2 o \rightleftharpoons co_2 + H_2$$

This reaction is the controlling equilibrium reaction for the production of carbon monoxide or carbon dioxide. At temperatures of $1200^{\circ}F$ and above, carbon monoxide is the primary product, while at $350^{\circ}-400^{\circ}F$, carbon dioxide is the principal product.

Five important parameters to be considered in steam reforming are the steam/carbon molar ratio, the reactor bed temperature, the space velocity, preheat temperature, and catalyst activity and life. Thus the composition of the gases leaving the reforming reactor is dependent on these factors.

In preliminary experiments it was found that methanol and gasoline mix over a wide range of composition, while diesel fuel and methanol form two immiscible layers. Only the lighter fraction of the diesel fuel appears to dissolve in the methanol. Thus it is difficult to define diesel fuel contamination, as it depends on the manner of mixing and the duration of contact between the two phases. In any case the light end of diesel fuel will be similar in composition to gasoline.

It was decided to study a 90/10 methanol/gasoline mixture. The relatively high gasoline percentage was chosen so that any changes in product gas composition due to the presence of gasoline could be measured with reasonable accuracy. Also, if any carbon deposition on the catalyst were to take place, it should be noticeable quite soon, i.e. within a few hours.

2.2 Test Equipment and Test Procedure

The test system is shown schematically in Fig. 2-1. An actual photograph showing the steam reformer is shown in Fig. 2-2. An Inconel reactor with 2.469 inches inside diameter (2-1/2" nominal pipe, sch 40) by 24 inches length was fabricated to fit into an electrically heated furnace. The reaction chamber contains the test catalyst.

The fuel feed tank was filled with premixed methanol/gasoline mixture. Fuel flow as well as water flow were measured using calibrated rotameters in series with orifice meters. Separate electrical heaters preheat and vaporize the reactants. The mixed vaporized fuel and water streams flow downward through the catalyst bed, through a water cooled heat exchanger, through a refrigeration unit, through a condensate collector and then to the atmospheric vent. The reactor has thermocouples to monitor the wall and catalyst temperatures as well as reactant and product temperatures. A sample line after the gas cooling apparatus provides a continuous sample to the gas analyzer for the determination of hydrogen, carbon dioxide, carbon monoxide and volatile hydrocarbon gases.

3.0 RAW MATERIAL SPECIFICATIONS

3.1 Fuels

3.1.1 Methanol

Technical Grade A (procured from Southland Industrial Products of Los Angeles, CA).

3.1.2 Unleaded gasoline, Indolene Clear, Federal test fuel. The chemical composition as determined by Truesdail Lab in L.A. is as follows:

Carbon	83,96%	
Hydrogen	83.96% 13.60% 0.036%	Wt. Percentage
Sulfur	0.036	
Paraffins	70*	
Oletins	8"	Vol. Percentage
Aromatics	33.	

3.2 Catalysts

Four catalysts were evaluated over a range of operating conditions.

The physical and chemical characteristics of these catalysts are given in Table

3-1. Three of these catalysts, namely T-2107-RS, G-66 B-RS and ICI 52-1 are

classified as low temperature shift conversion catalysts. Girdler G-56B represents
a steam reforming catalyst for hydrocarbons.

Low temperature $(480-500^{\circ}F)$ and low steam/carbon monoxide ratios are primary objectives for the operating conditions under which these catalysts would perform best in commercial applications. Copper/zinc oxide combinations have been found to be the most effective catalysts wherein the carbon monoxide conversion to carbon dioxide and not to methane or carbon is desired. Within this combination copper is the active catalyst and zinc oxide is the so-called "spacer". The role of zinc oxide is to maintain the copper catalyst as small crystallites and reduce the crystallite growth (thermal sintering) under operating conditions. Small crystallites of copper are much more desirable than large ones because of the higher surface area (hence greater activity) possessed by numerous small catalyst sites. Alumina is also used as a spacer with zinc oxide. Alumina and zinc oxide are different in terms of their aging properties, however. Alumina is an inert oxide which will maintain its oxidation state and structural integrity under these operating conditions (reducing atmosphere and temperatures <570°F) nearly indefinitely. Zinc oxide on the other hand will, although much slower than copper, grow slowly in crystallite size with time thus allowing the copper crystallites to grow also. In addition, zinc oxide is slowly reduced to zinc which will then alloy with copper forming brass. These changes also alter the pore size of the catalyst. Different catalyst preparation techniques have altered the aging processes of these catalysts but prolonged operation of these catalysts at temperatures above their limit (610°F) in the water-gas shift reaction will reduce the lifetime of low temperature operation.

When these low temperature shift catalysts are applied to the steam reforming of methanol, the catalysts are operating under different conditions and catalyzing different reactions. Although some shift reaction probably takes place $(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2) \text{ the basic reaction CH}_3 \text{ OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{3H}_2 \text{ is similar.}$

When hydrocarbons such as gasoline are mixed with methanol and this solution is steam reformed conditions different than those used in simple steam reforming of methanol are required. The steam reforming of hydrocarbons requires carbon-carbon bond breakage as well as carbon-oxygen bond formation and therefore follows a different mechanism than the methanol reaction. Different catalysts promote these types of reactions compared to the catalysts effective on the simpler methanol reaction. Further, gasoline is composed of a mixture of hydrocarbons and different carbon-carbon bond strengths, i.e., paraffinic, olefinic and aromatic (including some polynuclear aromatics) with single, double and conjugated bonds respectively. The breakage of these carbon bonds becomes progressively more difficult with the polynuclear aromatics being the most inert. In the attempt to steam reform a methanol-gasoline solution (90/10 wt) at temperatures well below those used in steam reforming of hydrocarbons, the use of low temperature shift catalysts, with slight modifications, was explored. Since the major difficulty in the initial reaction of gasoline is the breaking of carbon-carbon bonds without forming soot the combination of more alumina and higher steam to carbon ratio seemed necessary. In addition to being more stable at higher temperatures, alumina is more acidic than zinc oxide thereby aiding in the initiation of carbon-carbon bond breakage. The series of catalysts which would help bear out the alumina effect was G66B (no alumina), G66C (A1/Cu = 1/1.9), T-2107 (A1/Cu = 1/1), and 52-1 (A1/Cu = 1/1.6). At operating conditions above the manufacturer's suggested temperatures for these shift catalysts the low temperature shift activity may be reduced but the effect on the steam reforming of methanol/hydrocarbon solutions has no precedent from which the manufacturers are able to predict activity or durability. The relatively

unchanged activity of the catalyst T-2107 after 25 hours of steam reforming at various temperatures ranging to as high as 1200°F (exit) indicates that the activity of this catalyst for steam reforming the methanol solution is not dependent on all the same parameters that the shift activity is. Because of the range of temperatures, the accumulated time of operation and the apparent retention of activity compared to the other catalysts, catalyst T-2107 seems to be the best choice for duration testing. The ability for it to maintain activity is presumed to be a combination of high alumina content and low zinc content but other catalysts should be tested before the mechanism can be clearly understood.

4.0 PROCESS PARAMETRIC STUDY

4.1 Results and Discussion

The test data was recorded by two methods:

- o A digital data acquisition system was used to record test data on magnetic tape cassettes for post-run computer data reduction.
- o Manual entries into log sheets were made for operator and engineering observations.

Tables 4-1, 4-2, 4-3 and 4-4 show the measured and reduced data for the steam reforming of a mixture of methanol and gasoline (90/10% by weight) using catalysts T-2107-RS, ICI-52-1, G-66B-RS and G-56B. The steam reformer system was operated over a range of molar ratio of steam to carbon of 1.5 to 15.0 and over a reactor bed exit temperature range of 450 to 1150°F. The correlations and interactions between hydrogen yield, reactor bed exit temperature, steam to carbon ratio, residual gaseous hydrocarbons, carbon monoxide, and soot formation for each catalyst tested are discussed below under respective sub-sections.

4.1.1 Hydrogen Yield

The hydrogen yield in these test runs is defined as the ratio of the actual amounts of hydrogen produced under the test conditions—to the maximum amount of hydrogen that could have been produced from the input fuel for 100% conversion of both methanol and gasoline. This ratio is expressed as

where the square brackets indicate dry volume percentages in the product gas.

It should be noted that 19% of the total carbon input comes from the gasoline.

Figures 4-1, 4-2, 4-3, 4-4 and 4-5 show the correlation between hydrogen yield, reactor bed exit temperature and steam to input carbon molar ratio for catalysts

T-2107, 10152, G-66B-RS, G-56B and all these four catalysts together respectively.

From Figure 4-1 through 4-3 it is evident that for every 100°F increase in reactor bed temperature there is 3.8% decrease in direct hydrogen yield. It is also apparent that as the steam to carbon ratio is increased, the hydrogen yield increases. The decrease in hydrogen yield with increase in temperature or decrease in steam to input carbon molar ratio is due to the water-gas shift reaction.

In Figure 4-1 the areas enclosed by $A_1A_2B_2B_1$, $B_1B_2C_2C_1$ and $C_1C_2D_2D_1$ show the hydrogen yield with respect to bed exit temperature for steam to carbon ratios of 1.5, 3.0 and 6.0 respectively. The variation in space velocity accounts for the spread of data for the same steam to carbon ratio. The same observation holds true for the Figures 4-2 through 4-4.

Figures 4-1 to 4-3 also indicate that the hydrogen yield is higher with catalyst T-2107-RS than with IC1-52 and G-66B-RS under identical reactor bed exit temperatures and steam to carbon ratios.

The hydrogen yield for catalyst G+56B (Figure 4-4) indicates that this catalyst has very little activity below $1000^{\circ}\mathrm{F}$. This was to be expected as G-56B is a steam reforming catalyst for hydrocarbons. The hydrogen yield increases rapidly with an increase in temperature above $1000^{\circ}\mathrm{F}$.

Figure 4-5 shows the data for all four catalysts on one plot. As such it is a generalized plot of hydrogen yield vs. reactor bed exit temperature. This plot shows how the data points can be grouped under steam to carbon ratios of 1.5 (area $A_1A_2B_2B_1$), 3.0 (area $B_1B_2C_2C_1$) and 6.0 (area $C_1C_2D_2D_1$). The hydrogen yield is strongly dependent on steam to carbon ratio and on the reactor bed exit temperature, and not so much on the catalyst.

It should be noted that the plots of

do not represent the ultimate yield of hydrogen. The product may be cooled down to 400° F and passed over a low temperature shift catalyst bed to convert most of the CO to more hydrogen.

4.1.2 Gaseous Hydrocarbons

The gaseous hydrocarbon fraction is defined as the ratio of the moles of hydrocarbons in the product gas stream to moles of output carbon, where the latter are the total moles of carbon monoxide, carbon dioxide and hydrocarbons in the product gas stream. The gaseous hydrocarbon fraction is essentially all methane. Figure 4-6 indicates the correlation between the gaseous hydrocarbons, the reactor bed exit temperature and soot formation. Data points with soot formation are shown by shaded symbols.

If all the gasoline present is converted to methane, and none of this methane is steam reformed to hydrogen, then the maximum methane will be 19.4% for a 90/10% by wt. methanol/gasoline mixture. This is shown by the dotted line in Figure 4-6. So for values of methane below 19.4%, we may assume that some of this methane has been steam reformed into hydrogen. For values of CH_4 above 19.4%, we may assume that some of the methanol is converted to methane. This explanation also applies to column of $CH_4/.1914$ $CO+CO_2+CH_4$ in Tables 4-1 to 4-4.

The occurance of soot formation was determined from the amount of soot particles collected in the condensate from the product gas. This soot formation was rated on the scale of 0 to 10, zero being soot free and 10 representing an appreciable amount of soot. This qualitative rating is tabulated in Tables 4-1 to 4-4 for each test run. The data points with soot formation are marked with shaded symbols in Figure 4-6.

The data points in the zone below the solid line are essentially soot free for steam carbon ratios above 6.0, while most of the data points in the zone above the solid line have varying degrees of soot formation for S/C ratios below 3.0. The negative slope of the solid line indicates that more methane is steam reformed at higher temperature. This plot also indicates that soot formation is accompanied by higher methane contents in the product gas stream.

4.1.3 Carbon Monoxide

Figure 4-7 shows the effect of reactor bed exit temperature and steam to carbon ratio on the carbon monoxide concentration. It also identifies the data points with soot formation by shaded symbols (as discussed in Section 4-2). From this plot it is evident that carbon monoxide concentration increases as the reactor bed exit temperature increases or as the steam to carbon ratio decreases. This is obviously in line with the equilibrium of the water gas shift reaction.

4.1.4 Liquid Hydrocarbons in Condensate

Some of the condensate from the product gas had an oily film or oily droplets floating on top of the water level while other samples were essentially oil free. Perhaps a better description of the oil might be a yellow liquid hydrocarbon. This oil formation was rated on a scale of 0 to 10, zero being oil free and 10 representing an appreciable amount of oil. This qualitative rating is tabulated in Tables 4-1 to 4-4 for each test run. A rating of five might represent on the order of a percent of the gasoline throughput.

Figure 4-8, a photograph of four condensate samples taken from test runs with exit temperatures of 600, 650, 700 and 750°F with catalyst T-2107-RS indicates very clearly that as the reactor bed exit temperature increases, the yellowish coloration caused by the presence of oil droplets decreases. An analysis

of this yellow liquid hydrocarbon showed that it is similar to the heavy end of the gasoline. It proved to be very difficult to obtain representative condensate samples in short duration runs. The samples in Figure 4-8 were in fact from the 100 hour test of catalyst screening.

4.2 Conclusions

The experiments described above lead to the following conclusions:

- 1. It appears to be possible to gasify the gasoline in the methanol during steam reforming of the mixture. The gasoline is almost totally converted into methane. Trace amounts of the gasoline are converted into a yellow liquid hydrocarbon that is probably gaseous at 300°F (to be confirmed) and condenses out at room temperature. The presence of these trace amounts of hydrocarbons should not affect fuel cell operation at 300°F or above.
- 2. The above results can be obtained at temperatures in the range of $650-750^{\circ}F$, at steam to carbon molar ratios of approximately 5, and at input space velocities of 1600 hour^{-1} (STP), utilizing catalyst T-2107-RS.
- 3. Soot formation takes place at temperatures below $650-750^{\circ}F$ and/or at steam to carbon ratios below 5.
- 4. It is difficult to get good data on soot and residual liquid hydrocarbon formation in short duration tests of a few hours. To test the validity of the above results, and also obtain an indication of the stability of the catalyst, a long duration test is essential.

It was decided to utilize catalyst T-2107-RS for the 100 hour test because of its good performance over a wide temperature range, and because of its apparent high temperature stability.

5.0 100 HOUR TEST

5.1 Test Procedure

The process feasibility was demonstrated by operating the steam reforming

system continuously for one hundred hours without any major problems and by shutting the system down voluntarily.

The process schematic and the test equipment for this test were the same as those reported in Section 2.0 except thermocouple 68 was relocated to the top of the bed in the gaseous phase region. The reactor was filled with a new batch of catalyst T-2107-RS up to a bed height of $10^{\prime\prime\prime}$. The catalyst pellets were of $3/16^{\prime\prime\prime}$ x $3/16^{\prime\prime\prime}$ size and the weight of the catalyst was 2 lbs (896 gms). The test was started on 5/9/77 (Monday) at noon. The reactor bed exit temperature was measured by TC-55 at one inch from the bottom of the catalyst bed. This thermocouple was located inside the thermovell in the center of the reactor.

For the first seventeen hours the reactor bed exit temperature was controlled at 630°F (the maximum temperature recommended by the catalyst manufacturer for low temperature shift conversion) and at a steam to carbon molar ratio of 3.8. However, at these operating conditions liquid hydrocarbons were found in the condensate stream indicating a portion of the gasoline in the feed was neither steam reformed nor converted to gaseous hydrocarbons. To reduce these liquid hydrocarbons the steam to carbon molar ratio was increased and decreased to 5.2 and 2.5 respectively, but the effect was nil so after 27 hours of operation the reactor bed exit temperature was raised to approximately 690°F. At this temperature the amount of liquid hydrocarbons in the condensate had decreased, but was still appreciable. So after 39 hours reactor bed exit temperature was raised to 770°F and the steam to carbon molar ratio was varied from 3.8 to 5.1. Finally after 65 hours of operation the reactor bed exit temperature was raised to $820^{9}\mathrm{F}_{\star}$ and the steam to carbon molar ratio was increased from 3.8 to 4.7. At these operating conditions the liquid hydrocarbons in the condensate stream were completely eliminated. The test was terminated voluntarily after 102 hours of continuous operation. Figure 5-7 shows the variation in temperature with time (to be discussed more later).

Figures 5-1 and 5-2 show the variation in space velocity and steam to carbon molar ratio for 100 hours of test operation. The average space velocity was 1050 hr^{-1} and the steam to carbon molar ratio was varied from 3.8 to 5.2.

Space velocity is defined as the volumetric rate of flow of the input gases, measured at standard temperature and pressure, divided by the volume of the catalyst bed, expressed as hours⁻¹. Unless noted otherwise, this is the space velocity used in this report. Another definition of space velocity is in use based upon the output of hydrogen. This "hydrogen space velocity" may be defined as the volumetric flow rate of hydrogen product gas, measured at standard temperature and pressure, divided by the volume of the catalyst bed, expressed as hours⁻¹. Both space velocities are shown in Tables 4-1 through 4-4.

5.2 <u>Results and Discussion</u>. The test data was recorded by two methods:
A digital data acquisition system was used to record test data on magnetic tape cassettes for post-run computer data reduction. Manual entries into log sheets were made for operator and engineering observations.

Table 5-1 shows the measured and reduced data for the hundred hour test run. The steam reformer system was operated over a range of molar steam to carbon ratios of 3.5 to 5.2 and over a reactor bed exit temperature range of 600 to 820°F. The correlations and interactions between hydrogen yield, reactor bed exit temperature, steam to carbon molar ratio, residual gaseous hydrocarbons, carbon monoxide, hydrogen, carbon dioxide and space velocity are discussed below under respective sub-sections.

5.2.1 Hydrogen Yield. Figure 5-3 shows the correlation between hydrogen yield as defined in section 4.1 and the reactor bed exit temperature for catalyst T-2107-RS during 100 hours of test operation. From this figure it is evident that as the reactor bed temperature increases there is a decrease in the hydrogen yield due to the water-gas shift reaction. This confirms the earlier observation made in section 4.1.1. The hydrogen yield above 100% reported in

Figure 5-3 indicates soot formation in the reactor as the denominator term in the definition of the hydrogen yield assumes no soot formation. This soot formation was confirmed by the ratio of "carbon out" to "carbon in" given in Table 6-1. The comparison of Figures 4-1 and 5-3 indicates that under similar operating conditions namely reactor bed exit temperature, steam to carbon molar ratio and space velocity, a higher hydrogen yield was obtained in the 100 hour test run than in the short duration tests. The catalyst in the short duration tests was subjected to very high temperatures (1200°F), which in turn might have decreased the activity of the catalyst. This is probably the reason for the different results.

5.2.2 Gaseous Hydrocarbons

The gaseous hydrocarbon fraction, primarily CH₄ is defined in Section 4.2. Figure 5-4 shows the correlation between the gaseous hydrocarbons and the reactor bed exit temperature. From this figure it is apparent that the amount of gaseous hydrocarbons decreases as the reactor bed exit temperature increases. More methane is steam reformed into hydrogen at higher temperatures. This agrees with the observation made in Section 4.1.2. However, the comparison of Figures 5-4 and 4-6 indicates that under similar operating conditions the gaseous hydrocarbons formation was considerably less in the 100 hour test run than the short duration tests. As for hydrogen, the explanation probably lies in lower activity of the catalyst in the short duration tests due to high temperature exposure

5.2.3 Product Distribution

5.2.3.1 Experimental Measurements

Figures 5-5 and 5-6 show the composition of hydrogen, carbon dioxide, carbon monoxide and methane on a dry basis. It is evident from Figure 5-5 that the hydrogen yield remained at approximately the same level throughout the 100 hours of test operation. This indicates no reduction in activity of the catalyst T-2407 even at temperatures of $820^{\circ}\mathrm{F}$ and after long duration testing. It is also evident that the concentration of CO_2 , CH_4 and CO in the product gas also staved essentially constant.

5.2.3.2 Comparison of Experimental Results with Equilibrium Prediction

The theoretical equilibrium gas compositions for methanol-gasoline mixtures was calculated with the CFC 71 JANNAF Thermodynamic Equilibrium program and are plotted vs. steam to carbon molar ratio in Figure 5-9 for the reactor bed temperature of 800° F at a pressure of 1 atm. The experimental values of product composition (H₂, CO₂, CO, CH₄), as measured at a reactor bed temperature of 800° F and a steam to carbon molar ratio of 3.8 and 4.8, are also shown in Figure 5-9. This figure indicates that essentially all of the gasoline in the fuel is steam reformed to hydrogen, instead of hydrogenated to methane. This conclusion may be drawn from the low CH₄ concentration (0.8%) that was measured relative to the high CH₄ concentration predicted at equilibrium (8.5%).

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

For each mole of methane that is steam reformed there will be produced four moles of hydrogen and one mole of carbon dioxide, while two moles of water are consumed. If we subtract the experimental CH₄ concentration from the equilibrium value, and convert the difference into hydrogen by steam reforming, we obtain additional hydrogen, namely 26.1 volume percent. If we now add this extra hydrogen to the equilibrium hydrogen, it adds up to a value of 41.9 volume percent. This is in good agreement with the experimental value of 41.1 % H₂. In the same way, the water content would decrease to 43.0%, which compares well with an experimental value (derived) of 44.0%. In other words, the higher than equilibrium hydrogen can be explained in a satisfactory manner this way.

5.2.4 Reactor Temperature Profile

Figure 5-7 shows the reactor bed exit temperature measured by TC-55 at 1" above the bottom of the bed, as well as the gas preheat temperature measured by TC-68. The reactor bed exit temperature was raised from 600°F to 820°F in several steps as discussed in section 5.1. As the reactor bed exit temperature was raised by an external heat source, it also raised the preheat temperature of

the mixture of steam and fuel vapors. This was partly due to the reactor tube being only half full, and the top half thus acting as a prechamber. The gas preheat temperature was approximately 180 to 210° F higher than the reactor bed exit temperature. This temperature drop from the preheat zone to the bed exit thus provided part of the required heat of the endothermic reaction. It should be noted that the preheat temperature should be above the minimum soot temperature, i.e, the temperature below which soot will deposit on the catalyst. Even so, the preheat temperature was higher than needed.

The thermocouples TC-52 and TC-53 measure the wall temperature of the reactor at the 10" and 5" levels from the bottom of the reactor bed respectively. Thermocouple TC-55 measures the temperature of the catalyst bed in the center of the reactor at 10" and 5" level from the bottom of the reactor. Figure 5-8 shows the temperature gradient from the reactor wall to the center of the reactor at the same height of the reactor bed. It indicates that there is about $10^{\circ} - 20^{\circ} F$ and $20^{\circ} - 40^{\circ} F$ temperature drop from the wall to the center of the bed at the top and the middle of the reactor bed respectively. This small Δ T indicates a low heat transfer rate, which is consistent with the high preheat temperature discussed earlier.

5.2.5 Liquid Hydrocarbons in Condensate

As discussed in Section 5.1, some of the condensate samples had a yellowish looking oily film or oily droplets floating on top of the water level at lower bed temperatures. However, this was essentially eliminated as the temperature of the reactor bed was increased to 820°F. This oil represents the heavy end of the Indolene as an analysis indicated that 90° of the sample had a boiling point near the top end of the b.p. of Indolene. It was also found that the olefinic and aromatic content of the yellowish oil was higher than for Indolene.

6.0 CONCLUSIONS

- 1. Methanol contaminated with gasoline can be gasified in a conventional methanol steam reformer to produce a hydrogen-rich gas suitable for utilization in a phosphoric acid fuel cell. However, more severe operating conditions must be used and a slightly lower quality product gas is produced.
- 2. It has been found for a 90/10 methanol/gasoline (by weight) mixture that an operating temperature of 650-750°F is required. At these temperatures essentially all of the gasoline is converted into gaseous hydrocarbons, primarily methane. At 650°F traces of a light yellow hydrocarbon liquid are present in the product gas (after cooling). At 750°F this yellow oil is reduced to a minor trace, which at 820°F had totally disappeared. It appears that the yellow oil represents the heavy end of the gasoline. As such it should be a vapor at the fuel cell stack temperature, and should not intertere with the stack operation. However, experiments with an actual fuel cell are needed to confirm this.
- 3. A steam to carbon ratio of 3.8 was required to prevent soot formation and at the same time minimize the yellow oil in the condensate. A minimum temperature of 650° F was required to prevent soot formation. This implies that the minimum preheat temperature must be above 650° F. It appears that a lower gasoline content mixture can be processed with a lower steam to carbon ratio.
- 4. The T-2107 catalyst has shown good activity over a wide range of operating conditions, specifically temperature. It has retained its activity over the 100 hour test and shows good prospects for long life.
- 5. The carbon monoxide content of the product gas in the 100 hour test was 1.5 2.0%. This is somewhat above the 1% maximum level that is normally specified for a phosphoric acid cell. Operation at this higher CO level will result in somewhat lower performance. A definite way of

lowering the CO content is to cool the product gas to 400° F and to pass it over a small bed of low temperature shift catalyst (e.g. T-2107).

6. The sulfur in the gasoline (0.03 weight percent) will poison the T-2107 catalyst in time. The copper and zinc are converted into sulfides which are not catalytically active. To prevent this a bed of zinc oxide can be placed between the fuel/steam preheater and the steam reformer. Periodic replacement of the zinc oxide bed will insure that the bed does not become saturated.

The zine oxide will not remove all sulfur compounds, so that prolonged operation on gasoline contaminated methanol will slowly poison the catalyst with sulfur. A possible remedy would be to use high temperature shift converter catalyst (Fe), as FeS has catalytic activity. To confirm this further experimental work is required.

- 7. The following hardware changes to the conventional steam reformer should be made to enable operation on methanol that is contaminated with gasoline or diesel fuel:
 - a. Increase preheater size (to reach 650°F preheat)
 - b. add zinc oxide bed between preheater and steam reformer to remove sulfur compounds
 - c. increase the heat transfer rate to the steam reformer tubes to accommodate higher steam to carbon ratio (3.8) and a higher bed temperature (650-750 6 F)
 - d. possibly provide product cooling to 400°F and a secondary low temperature shift converter to reduce the carbon monoxide content below one percent.

Table 3-1

Physical and Chemical Characteristics of Test Catalysts

Trade Name	Girdler* T-2107-RS	Girdler* G-66B-RS	Girdler G-56B	ICI* 52-1
Particle Size, Inches	1/8" x 1/8"	1/4" x 1/8"	1/8" x 1/8"	1/8" x 3/16"
Bulk Density, lbs/cu.ft.	N/A	80	53 <u>+</u> 4	165
Chemical Analysis				
% A1	10.7	<0.06	74.0	5.29
% Cu	33.1	25.5	0.0	20.1
% Zn	16.3	51,9	0.0	35.2
% Ni	0.0	0.0	25.0	0.0

^{*} By Pomeroy, Johnston and Bailey Lab.

Table 4-1

Test Results of Steam Reforming of Methanol/Sasoline (90/10 % by Wt.)

Catalyst 7-2107 RS

															
Comments	041y	riis in Condensate	00	000	00	40	000	2-9	2	3.5	0	74	2.6		
3	Carbon	Forum.	00	007	0 7	70 6	4 M O	2	0	0 1	•	0	00		
** **	1949	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	48.3 50.9	67.5 71.0 67.4	68.6 69.1	89.5	84.1 82.5 82.0	117.3	101.8	52.6 52.8	64.0	53.5	66.7		• •
H ₂	3(CO+CO2+CH2)	**	82.3 76.3	76.0 82.0 73.2	72.5	70.3	71.4 71.5 69.0	63.0	82.3	76.2 80.8	78.9	78.4	82.5 76.2		
	CO+CO2+CH4	3·4	9.4	13.4 13.8 13.1	13.3	17.4	16.4 16.1 16.0	22.8 22.8	19.8	12.2	12.2	10.4	11.8		
		£,	3.0	4.0	4.2	5.6	5.2	7.5	5.7	3.7	3,7	3.1	3.4		
metric Prod Gas Compn.	(Dry Basis)	ខ	5.5	5.7	8.7	5.5	7.4	6.5	6.9	6.3	5.8	5.5	9.9		
Volumetric Product Gas Compn.	ž (Dry	c0 ₂	20.6	20,8 21.3 20.5	18.6	21.1	68.1 19.2 68.2 19.9 68.2 19.9	67.1 18.9	16.2	20.4	20.2	21.2	18.8		
<u> </u>		H ₂	71.1	69.5 71.1 68.7	68.5	67.9	68.1 68.2 68.2	67.1	71.1	69.5 70.8	70.3	70.1	71.2		
ure	Bed	r.	632	530 520 474	97.2	725	754 644 670	1110	2.90	.93 .93	56	1643	1046 056		
Temperature	Preheat	i.	556 556	590 520 524	£65	616	521 521 537	652 595	613	630 589	585	695	737 631	-	_
Moler	Rdtio of Steam	to Carbon S/C	2.7	6.3 3.1 1.6	3.1	16.0 16.0	3.1	3.1	3.1	3.1	6.3	15.5	80 6 0		
Rate	Water	Lbs/Ar	(1 (1	2 1 0.5	0.5	۳.		-3 (4	r,	2.2	2.0	5.0	2.0		
Flow Rate	Fuel	Lbs/Hr	1.33	0.5 0.5 0.5	0.5	0.3	0.0	4-	,	1.3	0.5	0.2	9.0 8.0		
Space Velocity in Hr -1	Out put		1054 1238	506 304 517	34 24 Æ 1\.	2853 2623	6 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1541	224	1333	067		008 96.	i only.	
Space Velo in Hr	Input (Fuel/	Water)	1939	15.15 80.02 12.02	906	3247	706 706	3615 1808	1780	2405	1616	3657	1580 2166	with park-mechanbi eniv.	-
lyst	Length	Inches	22	ener en ener en	77	end pro- pro-2 d	r 4 em em r 4 em em	7.13		::::	7.1	Ξ.			
Catalyst	Wr. in		1030 1030	0,07 10,30 10,30	05 01 05 01	10.0	6 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	960t	10.01	9,01 1930	1030	010:	9 12 919 919	Ar en U	
4	Scan No.		es C1	, ~		e ()		4						D V 1	
	Run No.		<u>*</u>	987	r.	,	3	Ų,	 -	3	 	;	·;		

Table 4-2

est Results of Steam Reforming of Methanol/Gasoline (90/10 % by Wt.)

Catalyst ICI-52-1

Comments	0417	In Condensate	7	000	0 00	
3	Carbon. Soot	Form.	7	707	0 4 4	
*B	.1949 (co+co,+cH.)	z a	65.8	70.0 68.9 75.6	72.0 74.6 72.0	
H ₂	3(00+007+034)	ĸ	81.3	74.9	79.3 74.0 70.5	
*	CO+CO2+CH4	7	12.8	13.6 13.4 14.7	14.0 14.5 14.0	
		5	3.7	4.2	4.5	
Volumetric Product Gas Compn.	% (Dry Basis)	8	7.0	5.3 6.3 5.9	21.0 4.0 19.0 7.6 16.6 11.0	
Gas C	(Dry	002	25	21.3 20.5 20.7	21.0 19.0 16.6	
Vol		± 2	71.0	69.2 69.3 68.9	69.0 69.0 67.7	
e in	Bed	ď.	261	258 600 604	557 483 589	
Temperature	Preheat	, L	650	638 652 594	512 512 512 512	
į	Ratio of Steam	to Carbon S/C	9.3	9.3 6.3	3.1 1.6 1.6	
Flow fate	Veter		۰	2 33		
er.	2 .5 2 .5			0.5	0.5	
Space Velocity	Output	(Rydrogen)	519	256 256 203	244 234 234	
Space Velor	Input (7ue)/	Mater)	2333	1166 2166 810	499 270 270	
Catalyst	Length		11	222	22 22	
ž	Fr. 1n	į	936	2020 2020 2020	2020 2020 2020	
	2	ġ	7			
	g		283	787	285	
						

Table 4-3

Test Results of Steam Reforming of Methanol/Gasoline (90/10 % by Wt.)

Catalyst G-668-RS

Comments	Films fin		110	Pr. of		
	Carbon Soot Forms.	00	٣	en en	r.	
ಕ ೆ	.1949 (CO+CO ₂ +CH ₄)	59.8 80.4	86.3	82,5	83.6	
H ₂	3(CO+CO ₂ +CH ₄)	4.7.5.	71.5	77.1	72.9	
*	сэ нсо₂ нсн ₂	11.6	16.7	16.1	16.2	
	3	3.5	5.3	5.1	5.1	
Volumetric Product Gas Compn.		_ 	5.7	6.2	6.1	
Gas Co	% (Dry Basia)	19.5	20.4	20.5	20.3	
Volu	¥ 2	69.9 69.3	5.89	58.2 59.8	2.0	
ure	Bed Exit	571	747	840 750	298	
Temperature	Preheat OF	681 665	/99	593 592	249	
A C	Ratio of Steam to Carbon S/C	3.1	j.	3.1	r 1	
Pate	Water in Lbs/Rr	2 2	~.		~	
Flow Rate	Fuel in Lbs/Hr			1.82		
Space Velocity in HF ⁻¹	Output (Hydrogen)	998	078	961 1832	1015	
Space Veloc	Input (Fuel/ Water)	3233 1799	2516	1799 2099	2516	
Catalyst	Length in Inches	11	=	22	<u></u>	
3	Wt. in Gas.	697	6977	6977	1.59	
	Scen No.		-			
	5 9	, j	305	į.	g g	

Table 4-4

Test Results of Steam Reforming of Methanol/Gasoline (90/10 % by Wt.)

Catalyst (-56B

ent s	001y F1134	Condensate	000	o	000	0	00							
Cyment s	Carbon Soot		000	0	000	-							-	
*5	.1949 (C0+C0 ₂ +CH ₄)	н	62.9 5.8 84.9	24.5	43.2 37.5 61.9	110.8	83.9 43.4							
H ₂	3(co+co2+cH4)	м	68.6 92.8 62.2	85.9	78.5 77.2 69.7	61.1	67.4							
** **	CO+CO +CH	ĸ	12.23 1.14 16.5	89.7	8.4 7.3 11.2	21.5	16.3							
ıcı		₹	6.0 5.8	1.2	2.5 2.2 3.9	7.6	5.4							
Volumetric Product Gas Compn.	% (Dry Basis)	8	17.7 3.7 22.4	8.6	6.8 20.5 8.0 20.0 9.7 18.8	18.3	16.8			_				
umetri Cas C	(D)	c ₀ 2	11.0 17.7 22.4 3.7 7.0 22.4	15.4		4.4	10.9 16.8 7.2 20.7						 	
Vol		Н2	67.3 73.5 65.7	89	70.2 69.9 67.7	64.7	66.9	·····					 	
ure	Bed Exit		1100 110 ⁷ 1106	97.	113. 1080 1020	1047	105							
Temperature	Preheat	•	496 478 414	627	519 576 676	553	510 514							
100	Patio of Steam	S/C	1.6 8.3 0.9	3.1	1.6	1.6	1.5							
Flow Rate	Mater fn	3	1 16 .66	2	2.5									
Flow	Fuel		0.35 1.33	-1	1.5						. 	· •••••		*
Space Velocity in R ⁻¹	Output (Hydrogen)		1473 862 1072	2211	1502 2408 3193	1336	1505		l only.					
Space Velor	Input (Fuel/	, , , , , , , , , , , , , , , , , , ,	2150 2473 1938	359.8	2165 3247 4330	2165	2145		a methano					
Catalyer	Leagth	I DC DC	8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	5.5	2.6.0	5.5	5.5		Tons are with pun				 	
Cata	ال الله الله الله الله		522 552 552	e ;	6 6 6 6 6 6	553	552		TUDS 374					
	Scan No.					.,	.1		,					
	5 9		į,	₹,			\$5.		į.	-1-1				

(100 Hour Test Rum) Table 5-!

Test Results of Steam Reforming of Methanol/Gasoline (90/10 % by Mt.) Catalyst T-2107-RS

Page 1 of 4

_										24	•														
c out x 100	c _{in}			82.3		83.2		90.2			76.3				£ 4.4		2.0	0.09	71.0	74.0	74.0			98.0	
, CH,	6761•	(CO+CO ₂ +CH ₂)		34.8	35.4	26.7		27.7			31.0				39.5		20.5	39.8	9.75	35.2	35.2			23.4	
Н2	3(CO+CO,+CH,)	1 1		97.9	94.5	6.86		6.56			101.2				127.5	,	7.711	1103	105.3	101.1	101.1			92.9	
7 HD	CO+CO +CH,	4		5.7	6.4	e i		5.4			4.04				7:7	:	6.	4		6.86	6.86			55	
nce		e d			×.	-	_	•			1.5				٠.	(0.7	×	, , ,	1.1					
Volumetric Produce Cas Compn.	(Dry Basis)	8		9.0	1.3	0.5		1.1			6.0				6.0		^ ·							1.1	
umetri Cas C		202		23.1	23	23.4		23.5			22.4				18.2	,	19.1	20.00	21.6	21.9	21.9			24.1 1.1	
Vol	H -	н		74.6	74.0	œ;;;		74.0			75.3			_	79.2	;	3.77	2.00	75.5	75.2	75.2	<u></u>		73.6	
ture	Bed	F.		525	450	785	622	629	625	629	633		641		074	645	474 436	100	702	402	669			\$ 1	
Temperature	Preheat	L		57.5	585	787	832 826	831	25 60 20 70 20 70	いけま	€ .1 .2		843	્યું છે. જે છે	0 or 0 or	37 30	~ a	6.46	8. 8.58	606	706			89 3 89 3	 6×
	Ratio	to Carbon S/C		5.2	80 °C) ac	ec ec	100	x x	8 C.	x.		3.8	20 CK	c 90 .	ac			2.5	2.9	4.2			x x	ac
Flow Rate	Water	Lbs/hr		5.5		1							e		:::		C 10) a	. 0	0.55				-	
Flo	Fuel	In Lbs/hr		0.45	5 10	0.45	: ; ; ; ; ;	0.45	\$;; = e	0.43	0.+5		0.45	ή (. Ο σ	57.0	·;;	0.315		,	0.3	0.41			€ 4, oʻoʻ	S.
Space Velocity in HR-1	Input	Light Here		746		.6.	107	1. 1 1 0. 1	70.7	1.70.			10-1	1.701	; • 0 :	. 76.	3	· ·	95	121	6.7 (7)		:	or of the second	
	apos.	į	1		- ·	•	.e. r.	,	• ₹	:				•	. :.		. .		17				,		•
	Ċ			· · ·		• :						1			•		•		-						

8	<u> </u>		1										2	25													_		—	~-
	, cl		2 28			2.46		97.7			91.0				92.4	83.0	9	00.00		95	,	5.6	0.16		9	0.11		. 	83.7	
⁷ 5	. 1949	(co+co ₂ +cH ₄)	25.8			25.0		19.5			25.7				25.3	7.47	25.0			25.2		7.57	63.6		5 75				30.2	
H ₂	3(CO+CO,+CH,)	1 7	45.4			91.5		93.0			7.76				93.5	70.0	0 %			92.5		0.0			117.6				97.76	
7,60	CO+CO, +CH,	, ,	5.02			4.87		3.79			5.0				4.94	7).+	70 %			٠ ٦٢		. ·	;		6.9				5.88	
duce		₹"						1.0			1.3				· -	•	-	:		1.3		•	· ·						7.1	
Volumetric Produce Gas Compn.	(Dry Basis)	8	7,			2.5		2.3			1.7	-			7.6	_				2.4		. T. C							1.3	
Jumetr	% (Dry	200	23.2			22.9		23.1			23.1				1.5.1	7.77	73.7			22.8	ć	33.4	7.77		7 61				22.8	
20		H ₂	74.1			73.3		73.6			73.9			,	7,5.0	9.	74.7			73.5	;	2,60	13.3		78.0				74.5	į
e in	Bed	į.,	869	683		678	747	752		752	757	753	3.50	756	6+1	758	761	761		756	9	0 7	7.67		7.70	783	776	781	782	4
Temperature	Preheat	•	961	868	903	901	596	962		796	963	096	961	096	904	965	963	196	096	096	796	961 961	957	626	928	955	953	953	556	455
	Ratio of Steam	te Carbon S/C	3.8	3.8	0 00	3.00	2.8	3.8		3.8	3.8	80.0	 		2.4	4.2	4.2	4.2	4.2	5.6	9.6	6.7	5.1	2:1	5.1	5.1	5.1	5.1	5.1	0 0
Flow Rate	Water	Lbs/hr	1.1			1:1	1.1	1.1		1.1	1.1	1.1			•	1.1	1.1	1.1	1.1	1.1	96.0		1.1	1.1	1.1	1.1	1.1	1.1		· ·
F10	Fuel fn	Lbs/hr	0.45	27.0	0.45	0.45	0.45	0.45		0.45	0.45	0.45	Ç, ,	0.45	0.41	0.41	0.41	0.41	0.41	0.31	14.0	0.41	0.34	0.34	0.34	0.34	0.34	0.34	0.34	
Space Velocity in HR ⁻¹	Imput (Fuel/Water)		1050	1050	1050	1050	1050	1050		1050	1050	1050	000	1050	1031	1031	1031	1031	1031	166	921	1030	1003	1003	1003	1003	1003	1003	1003	106.7
I	Scen No.		<u> </u>	32	33	7.	35	<u>~~</u>		33	80 5	<u></u>	2 -	77	43	77	4.5	9,7	7.7	27 ×	2 3	21	25	53	. 75	25	26	57	× 5	
	T.		800	2000	2100	200	2300	007	5/11/27	0200	8 8	3 8	3 5		200	008	 906	000	8 8	3 5	8 8	200	009	200	900	8	8	8 8	2300	200

	× 196											-			2	26						_								-		
	× ui			0.26				104.3		100.2				109.2	_			100.4			C	105.6					4,			23.53		
⁷ to	. 1949	(co+co ₂ +cH ₄)		25.7				28.1	,	72.1				24.3			;	36.9				64.3								00 1.7) ;	
H 2	3(CO+CO2+CH,)	.d		93.9				88.3	c c	92.0				58.7	_,		,	84.6		-		7.60					1 601			178;	•	
5	CO+CO, +CH,	3 N		٥.٠				5.47	d	· ·				4.74			•	61.	-	_	9	· ·				•	78			4.37	!	
luce		€						.; 										0.7							_							
Volumetric Produce (as Compn.	(Dry Basis)	8		1.5				3. 2.6		- 1.3				2.0				6.1 6				3.1						6:1			-	
lumet r	Z (Dry	202	ļ	4.60				23.3		77				24.1				23.9				23.8						· ·			15.0	
5		H ₂		73.8				72.6		. 3				72.7				72.2				72.8					ì	c. c.			×	
ure	Bed	T L		808		_		803		806	825	472	0	808	830	827		811	845	• • •	827	35.5	.; ; 200		842		·	i c	,		1//	2
Temperature	Preheat			1019	1016	1016	1017	1014	1015	1016	1014	1015	1014	1016	1013	1013	1014	1015	1015	1014	1012	101-	1010	1011	:008	1010	,	1012	# E E E	1110	+ 71.5 71.5	1 340
,	Molar Ratio of Steam	to Carbon S/C		3.8	8.5	3.8	3.8	3.8	nc ~	 	ص م م	 	 	8.7	œ.	3.8	80.7	œ. ,†	œ. .†	œ. . ₇	œ.	oc :	xc -,†	x.	œ.,	∞ .,	0	c a	c o		r oc	
Flow Rate	Water	Lbs/hr			1.:	1.1	1.1	1.1	1.1	1.1	Ξ.	7.7		1.1	1.1	1.1	1.1	1.1	1.1	1.1			·-·	1.1	<u></u>							
Flo	Fuel	Lbs/hr		0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	99	0.45	0.37	0.37	77.0	0.37	0.36	0.36	0.34	0.36	0.36	. 34	9,6	±	÷.	· · · · ·	0.36	÷ ;	Ξ :	 	
Space Velocity to HR-1	Input (Fuel/Water)			1943	1047	10-7	10.7	1047	1047	130rt	1047	7 7	1047	1015	1015	1043	1915	1011	1011	::6:			::0:	1011	e de la companya de l			*			7.5	
}	Scan No.			5.1	62	\$ \$;	45	ç	ن ا	no d	0.1		7.5	£.			42	1.5	¥		Ç ;	Y.	x,	or at	;	1	í ;		: 1	t -? F t	
	Time		f :	0100	0570	00₹ u	00.00	0200	0090	00:0	0.800	000	1190	1225	1110-1		1360	- C - C	96.	9(-	<u> </u>	(G. 5)			5	00.	\$		_		•	_

	Cout × 100				27			
				79.8	7.66	93.9	77.8	
	° НЭ	. 1949 (CO+CO ₂ +CH ₄)		45.5	28.7	29.2	9.2	
	3(c0+c0 ₂ +cH ₄)		131.0	91.1	92.9	98.1		
	CH,	CO+CO,+CH,	4	8.87	5.6	5.7	7.2	• • •
	Volumetric Produce Gas Compn.		ਲੋਂ	80	17.	1.5	œ:	
		Z (Dry Basis)	8	1.7	1.3	1.3	1.4	
	Gas C		200	16.8	24.	23.6	33	
	Λο		Н2	79.8	73.2	73.6	74.7	en e
	17.8	Bed Exit		772 780 786	783	787 788 781	778	
	Temperature	Prehest		975 973 970	676 896 876 876	979 979 978 979		* · · · · · • • · · · ·
	Molar Ratio of Steam to Carbon S/C		444 \$\$\$\$\$\$\$	င်တော်တာတော်	3 4 4 4 80 80 80 W	3.5	,	
	Flow Rate Water		Lbs/hr	222	- - - - - - - - - - - - - - - - - - -		0.78	
		Fuel 1n	Lbs/hr	0.36 0.36 0.36	0000	0.36 0.38 0.38	0.35	
Space Velocity	Space Velocity in HR ⁻¹ Input (Fuel/Water)			2011 1011 1011			2001	
-	_ [Scan No.		ज अ के त	 G& 5	6 6 0 C	G	
		ļ.		5755 5805 9405 1006	0011	1 400 1 400 1 7 0 0		·= == matter or = cop q

STEAM REFORMING OF METHANOL/ GASOLINE (90/10 BY WT.)

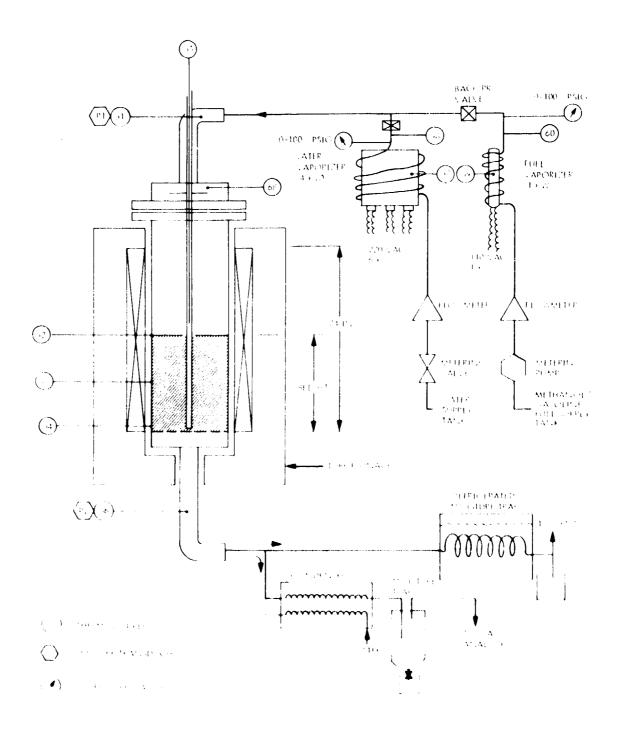


Figure 2-1 Schematic of Steam Reformer

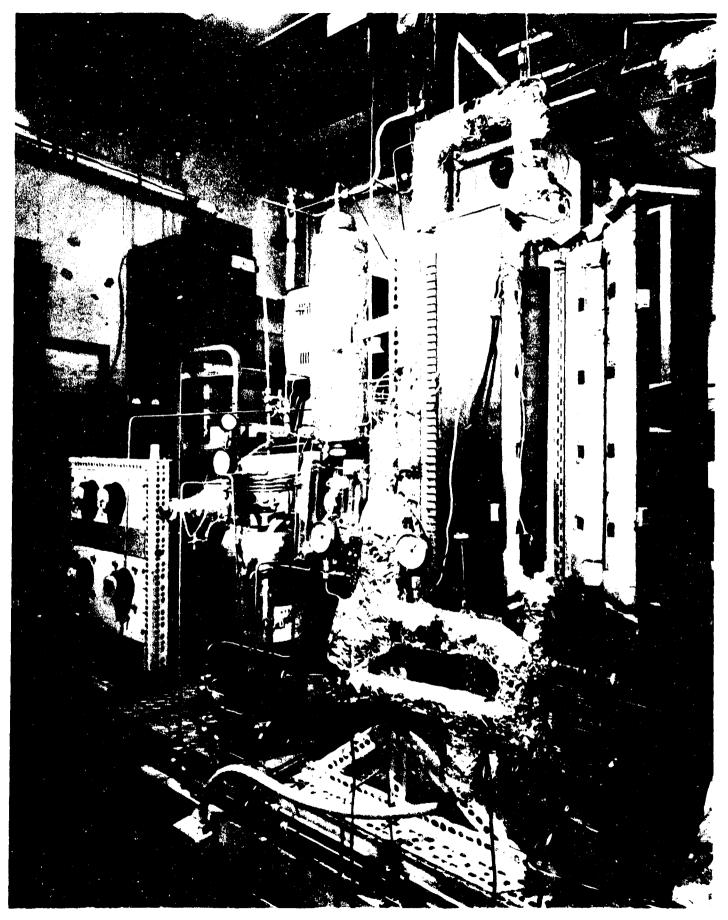


Figure 2-2 Photographic View of Steam Reforming System

STEAM REFORMING OF METHANOL/GASOLINE (90/10 BY WT.)

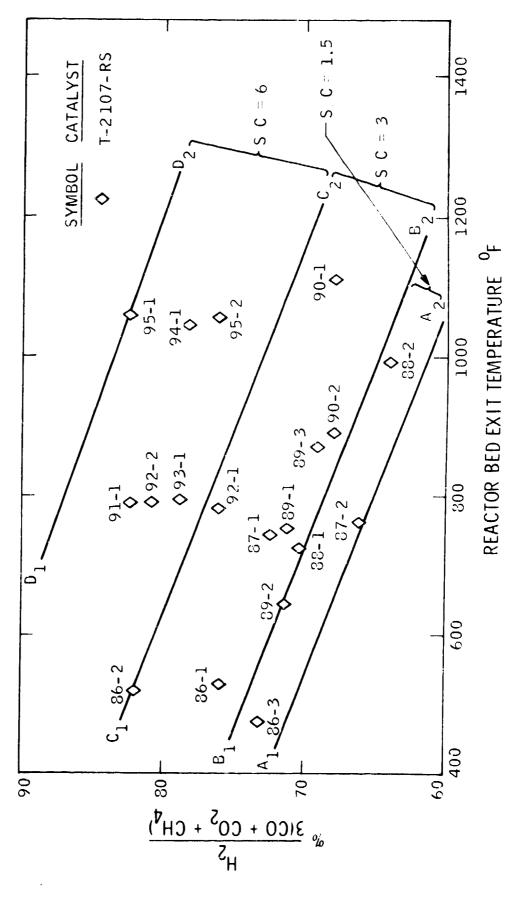


Figure 4-1 Effect of Reactor Bed Temperature on Hydrogen Yield

STEAM REFORMING OF METHANOL/GASOLINE (90/10 BY WT.)

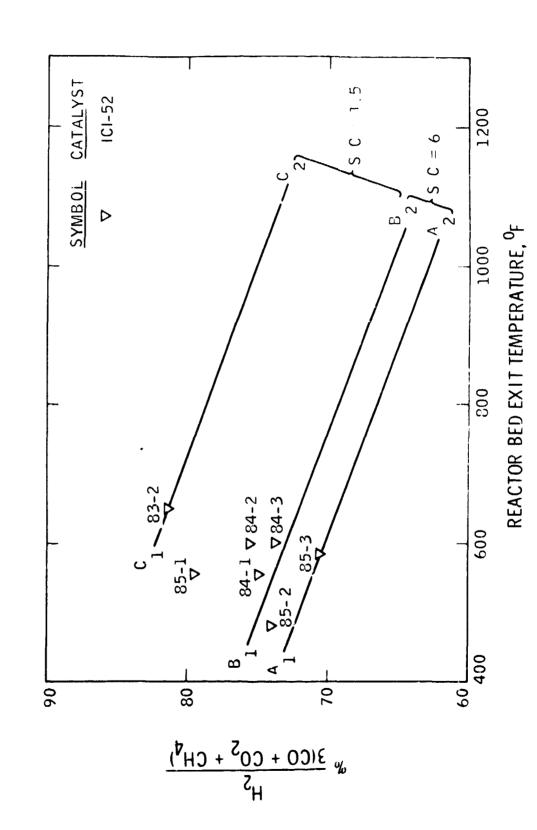


Figure 4-2 Effect of Reactor Bed Temperature on Hydrogen Yield



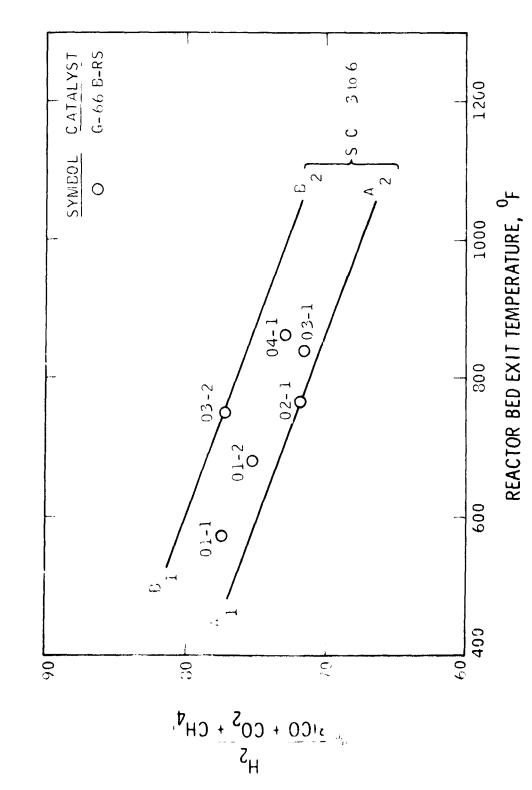


Figure 4-3 Effect of Reactor Bed Temperature on Hydrogen Yield



STEAM REFORMING OF METHANOL/GASOLINE (90/10 BY WT.)

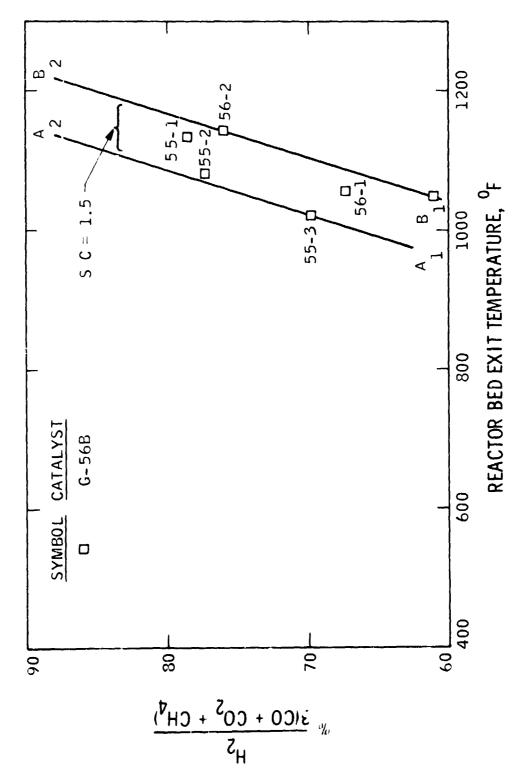


Figure 4-4 Effect of Reactor Bed Temperature on Hydrogen Yield



(90/10 BY WT.)

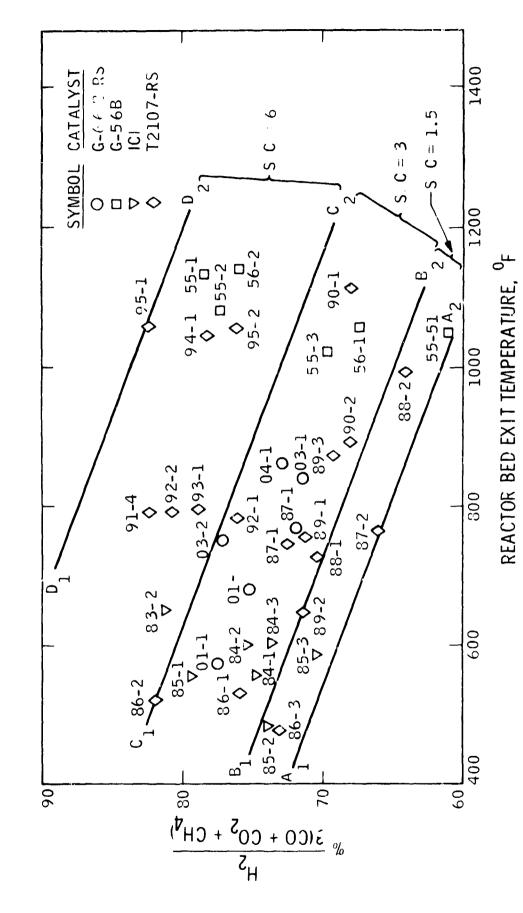


Figure 4-5 Effect of Reactor Bed Temperature on Hydrogen Yield



STEAM REFORMING OF METHANOL/GASOLINE (90/10 BY WEIGHT)

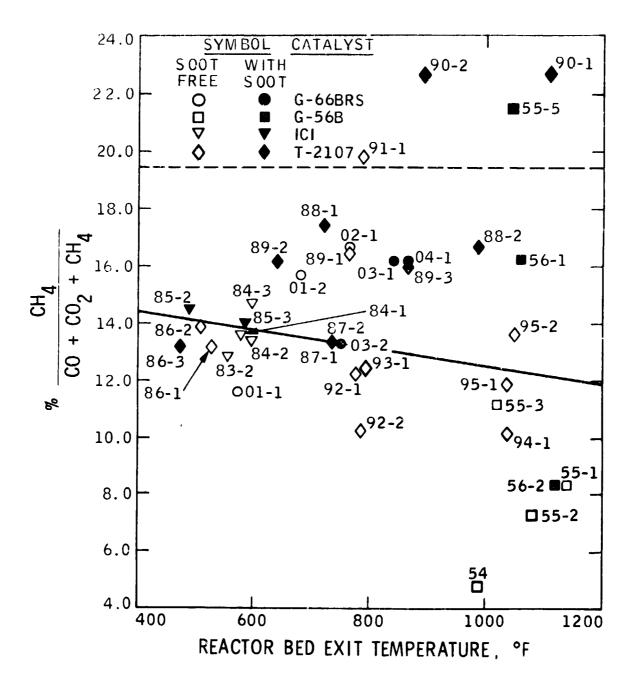


Figure 4-6 Effect of Reactor Bed Temperature on Gaseous Hydrocarbons

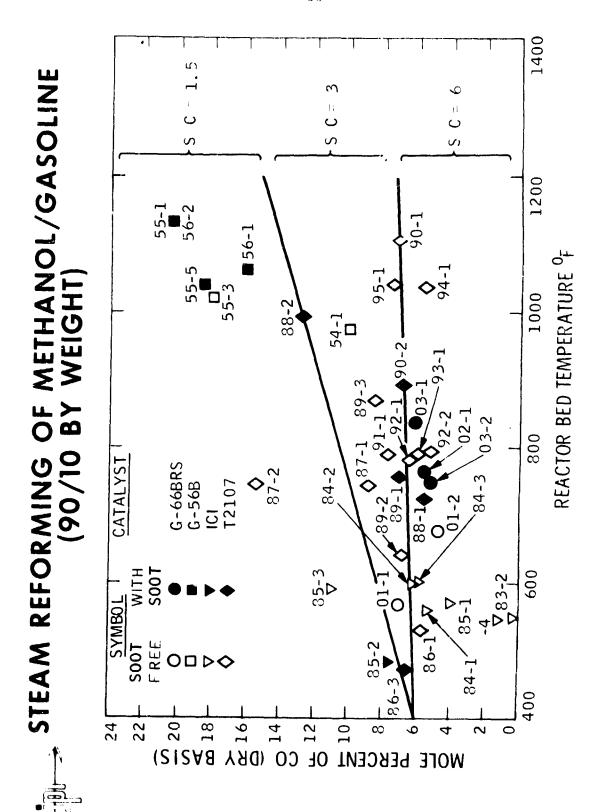


Figure 4-7 Carbon Dioxide Concentration (Dry Basis) During Process Parametric Study Tests

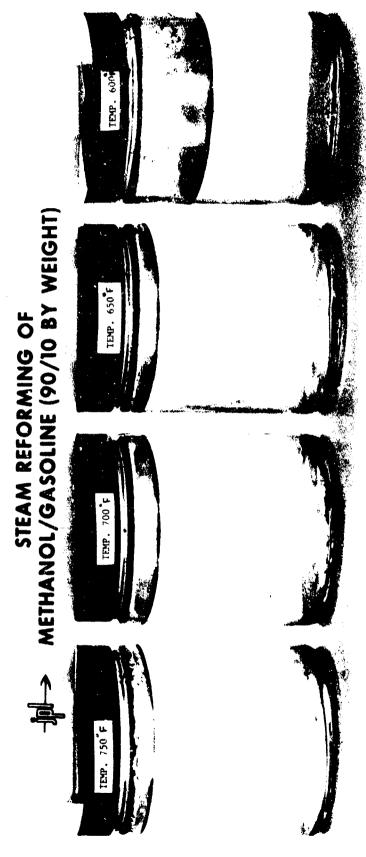


Figure 4-8 Effect of Reactor Bed Temperature on Lightd Pedrocarbons to combosate samples.

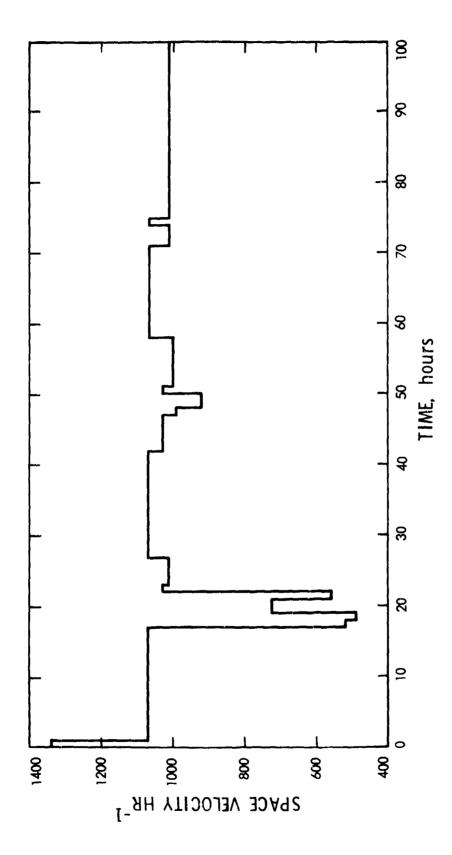


Figure 5-1 Variation in Space Velocity in 100 Hour Test

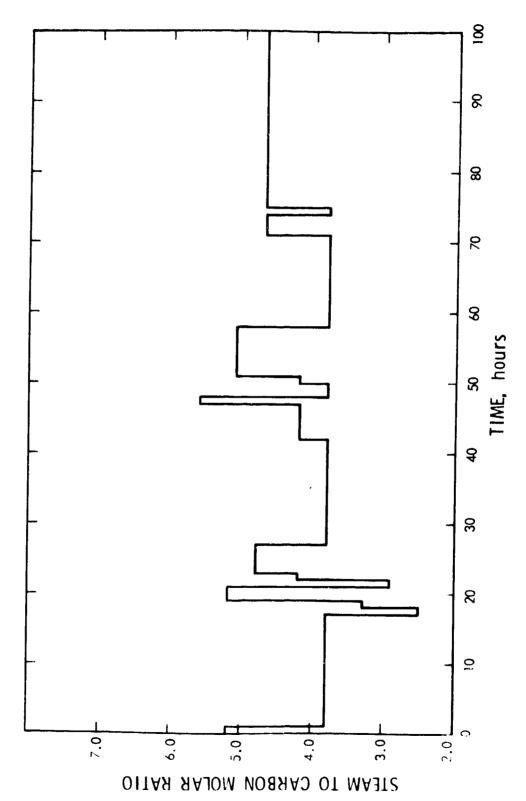


Figure 5-2 Variation in Steam to Carbon Molar Ratio in 100 Hour Test

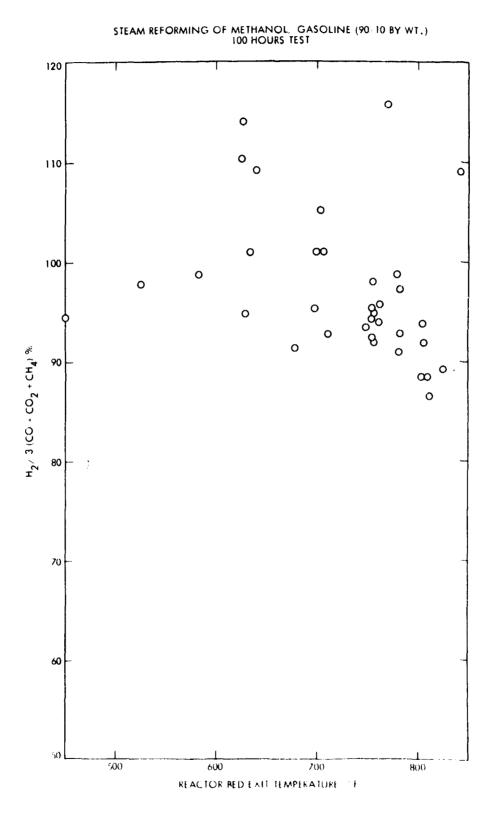


Figure 5-3 Effect of Reactor Bed Temperature on Hydrogen Yield

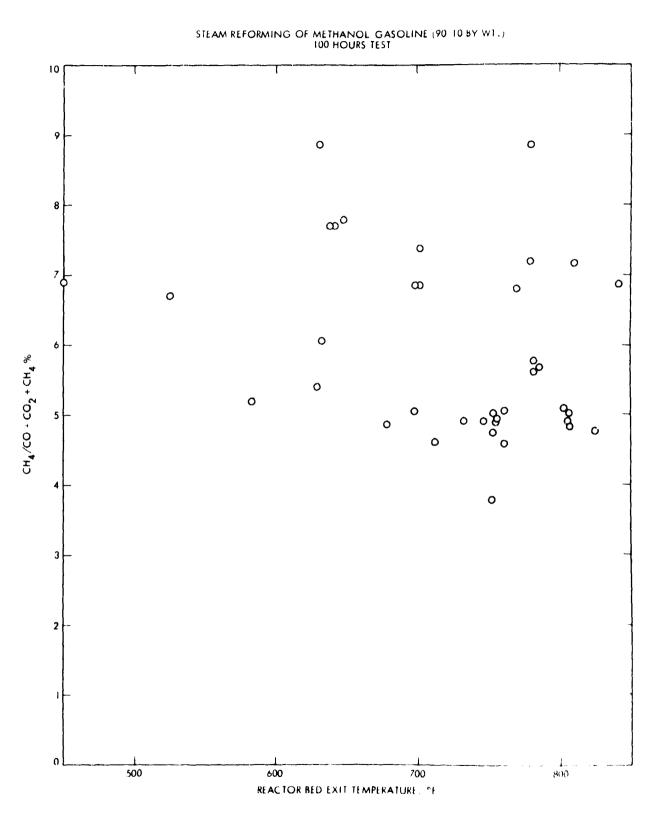


Figure 5-4 Effect of Reactor Bed Fxit Temperature on Gaseous Hydrocarbons

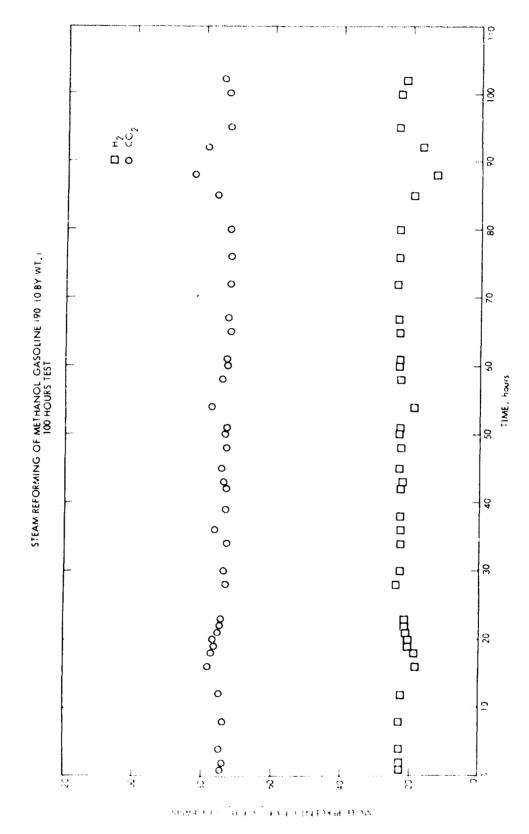


Figure 5-5 Carbon Dioxide and Hydrogen Concentration (Dry Basis) During 100 Hour Test

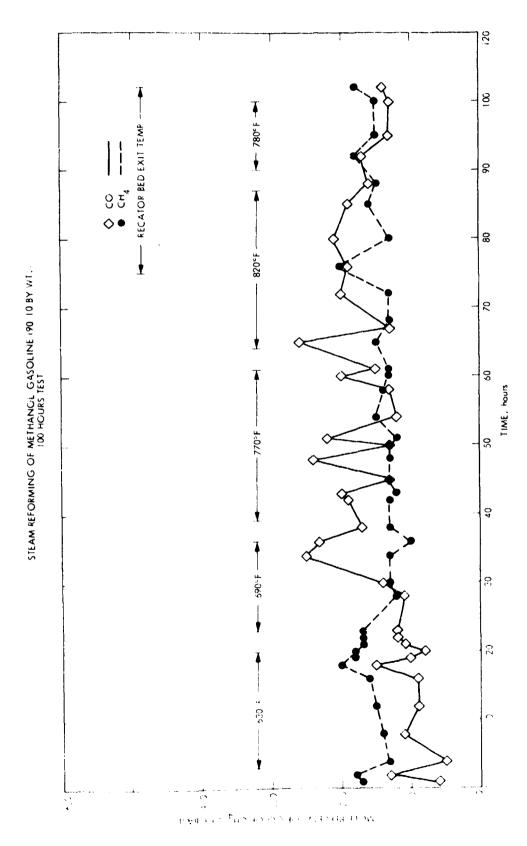


Figure 5-6 Carbon Monoxide and Methane Concentration (Dry Basis) During 100 Hour Test

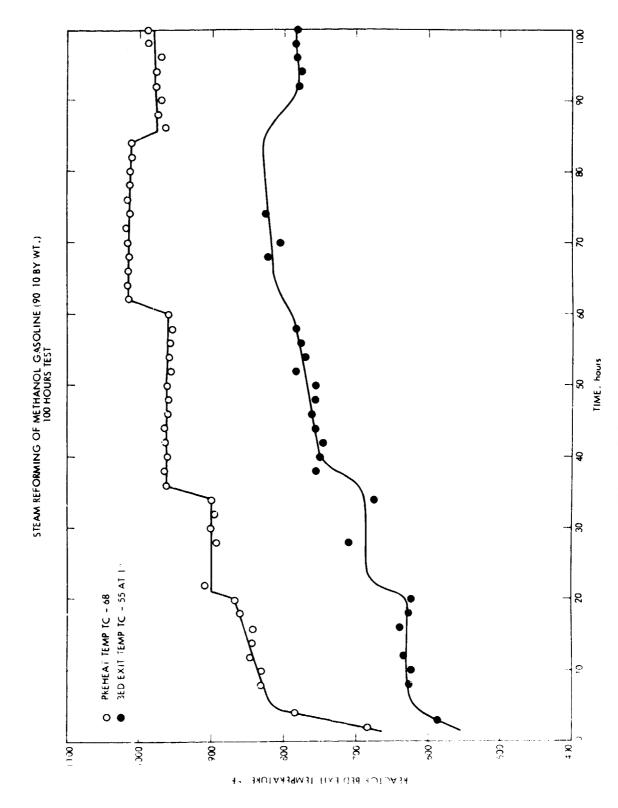


Figure 5-7 Bed Exit and Gas-Preheat Temperatures in 100 Hour Test

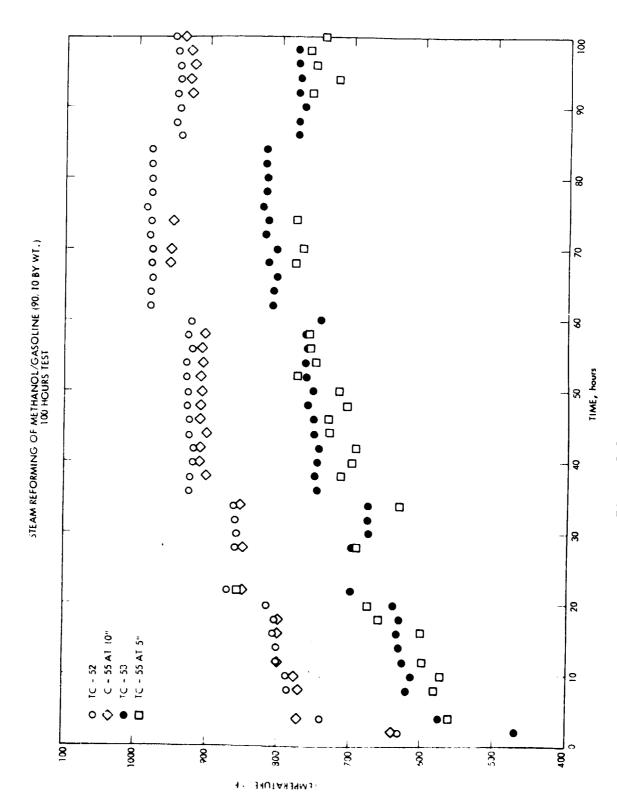


Figure 5-8 Reactor Bed and Reactor Wall Temperature Profile in 100 Hour Test

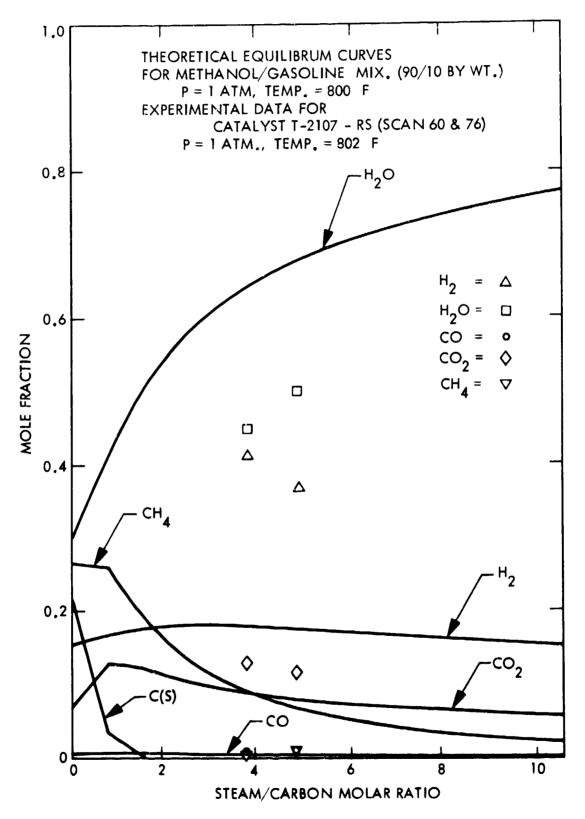


Figure 5-9. Product Distribution

APPENDIX

Equilibrium Product Composition of Methyl Fuel

APPENDIX

EQUILIBRIUM PRODUCT COMPOSITION OF METHYL FUEL

The equilibrium product compositions of 90/10 methanol/gasoline mixtures (by weight) have been calculated with the CEC 71 Computer program. This program is based on the minimization of Gibb's Free Energy of the System. A subprogram has been added to the main program to enable plotting of the equilibrium composition versus the input conditions such as steam to carbon ratio. The results of the program can be used further to calculate the yield in terms of product to fuel carbon molar ratio. The moles of hydrogen plus carbon monoxide produced per mole of fuel carbon input were also calculated. Such normalized data represents a good means for comparing yields.

The ranges of this survey are listed in Table A where the ranges of temperature, pressure, and steam to carbon ratio of the reactants are given.

TABLE A

RANGE OF OPERATING CONDITIONS OF STEAM REFORMING SURVEY

Pressure (atm): 1, 3, 5

Temperature (°F) 400, 600, 800,

1000, 1200, 1400, 1600

Steam to Carbon Molar Ratio: 0-15

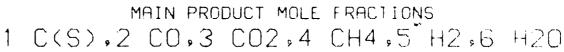
The main products at various steam to carbon ratios are given in Figures 1 to 21 in mole fractions and in Tables 1 to 21. In those figures, the unconverted water increases as the steam to carbon ratio increases. Methane decreases as the steam to carbon ratio and temperature increase. Pressure has only a small effect. The hydrogen yield at 400° F is very low. It increases very fast as the temperature is increased. At low temperatures the yield is not sensitive to steam to carbon ratio. As the

temperature increases further, the hydrogen yield reaches a maximum and then gradually decreases. Carbon monoxide decreases with an increase of steam to carbon, because carbon monoxide shifts to hydrogen.

The products can be normalized by expressing them as moles of product per mole of fuel carbon. The results of this calculation are given in Tables 22 to 42 as a function of temperature and pressure. The tables are tabulated in both weight and molar steam to carbon ratios. Those results are also plotted in Figures 22 to 42. The plots show that the normalized hydrogen plus carbon monoxide yield, reaches a plateau around a steam to carbon ratio of 2. This means that the maximum hydrogen yield can not be increased beyond a steam to carbon ratio of 2. The physical explanation of this fact that after the steam to carbon molar ratio reaches 2, the increase in hydrogen is only at the expense of a decrease in carbon monoxide. This gives an important reason for not using too much steam, as it requires energy to generate the steam. One must also consider the heat of reaction in this reactor, and express the amount of energy required in terms of mass of fuel that is needed. Sometimes, this energy can be supplied by a source of waste heat.

In other cases a fraction of the total fuel input must be used to produce a heat source. However, the efficiency of utilization of this heat depends on the size of the heat exchangers used etc. This is beyond the scope of this survey.

FIGURE 1.



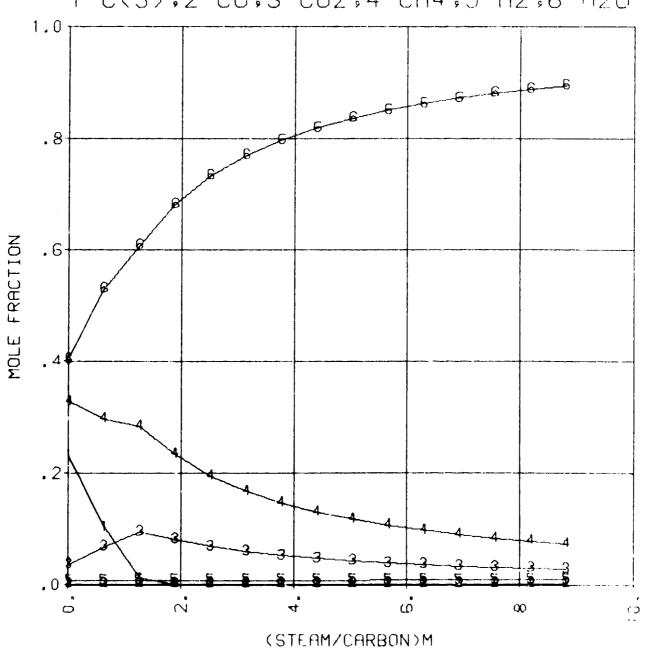


FIGURE 2.

SIEAM REFORMING OF THE THYL JUEL P-1, UOATM T= 600, F

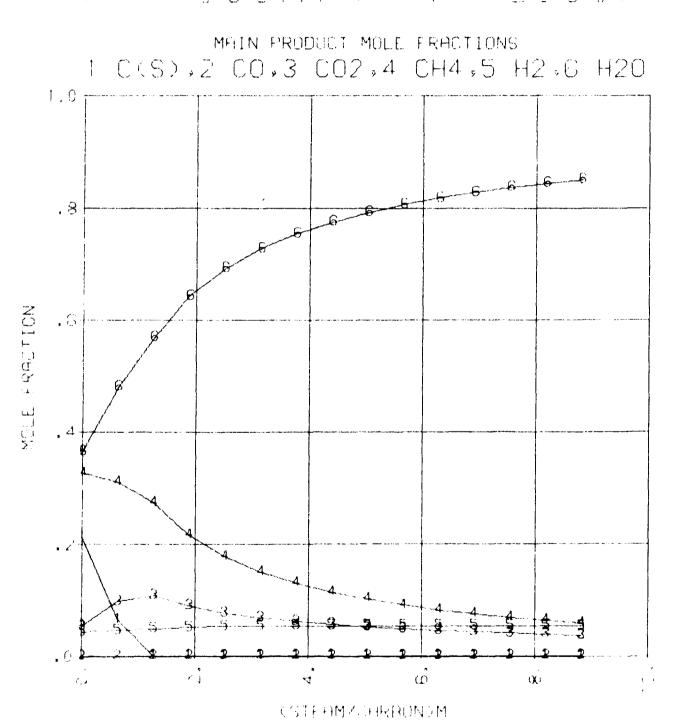


FIGURE 3.

STEAM REFORMING OF METHYL FUEL P = 1 . 00 ATM T = 800 F

MAIN PRODUCT MOLE FRACTIONS

1 C(S),2 CO,3 CO2,4 CH4,5 H2,6 H20

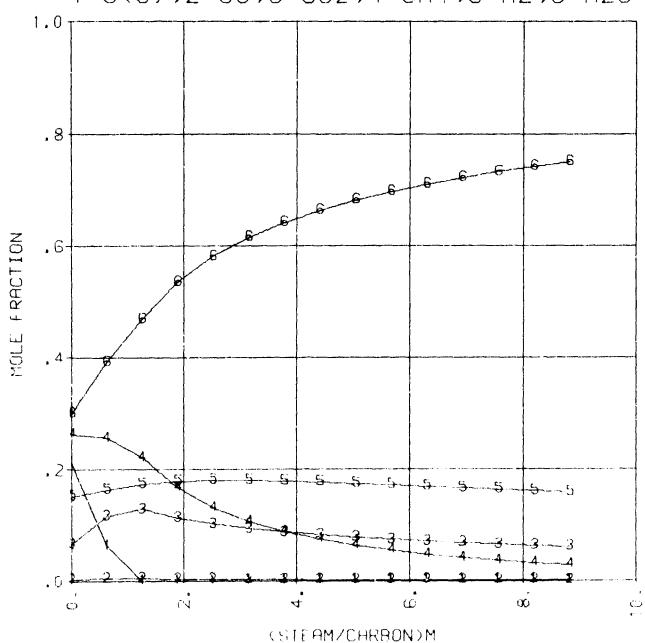
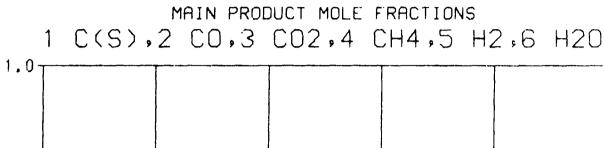
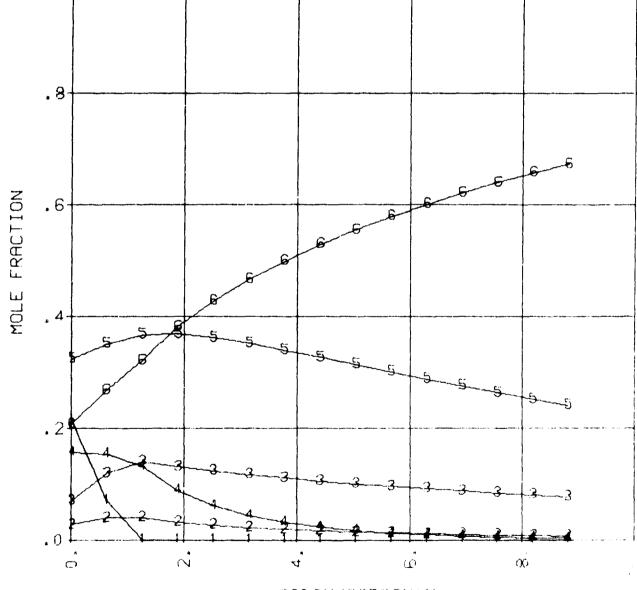


FIGURE 4.

STEAM REFORMING OF THE THYL FUEL





(STEAM/CARRON)M

FIGURE 5.

STEAM REFORMING OF THE 120 FUEL

main product mole fractions

1 C(S),2 CO,3 CO2,4 CH4,5 H2,6 H20

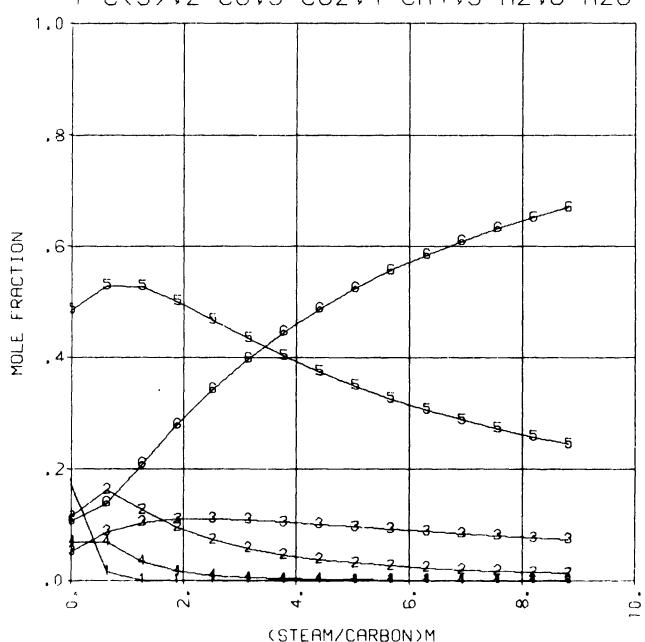


FIGURE 6.

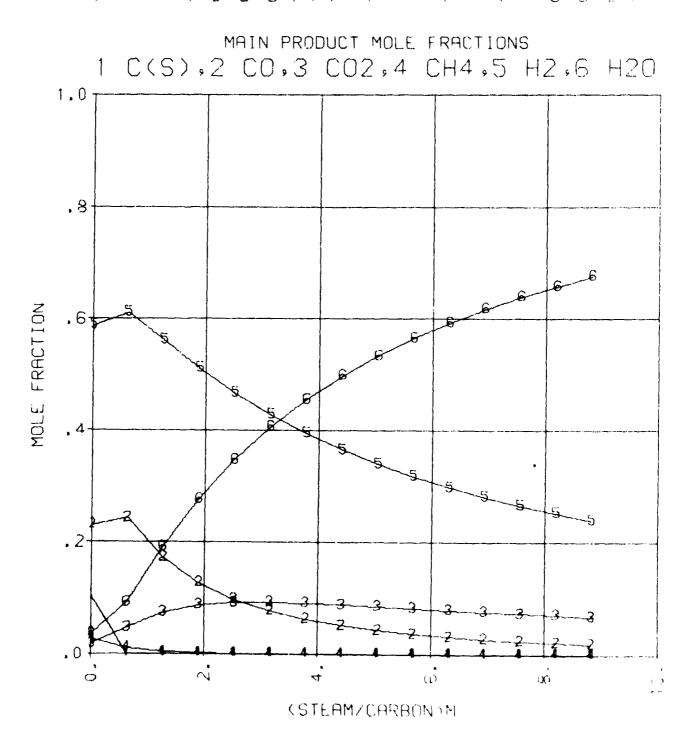


FIGURE 7.

STEAM REFORMING OF METHYL FUEL P= 1.00 ATM

main product mole fractions 1 C(S), 2 CO, 3 CO2, 4 CH4, 5 H2, 6 H2O

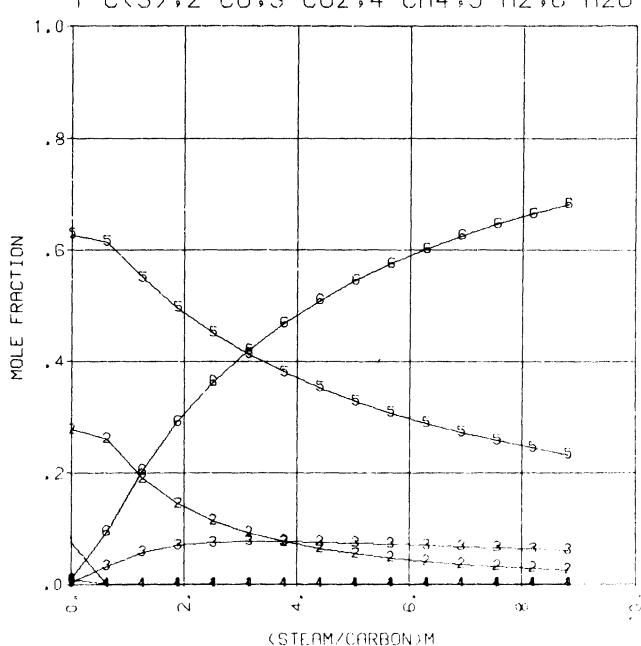


FIGURE 8.

STEAM REFORMING OF METHYL FUEL P= 3.00ATM OF TETHYL FUEL

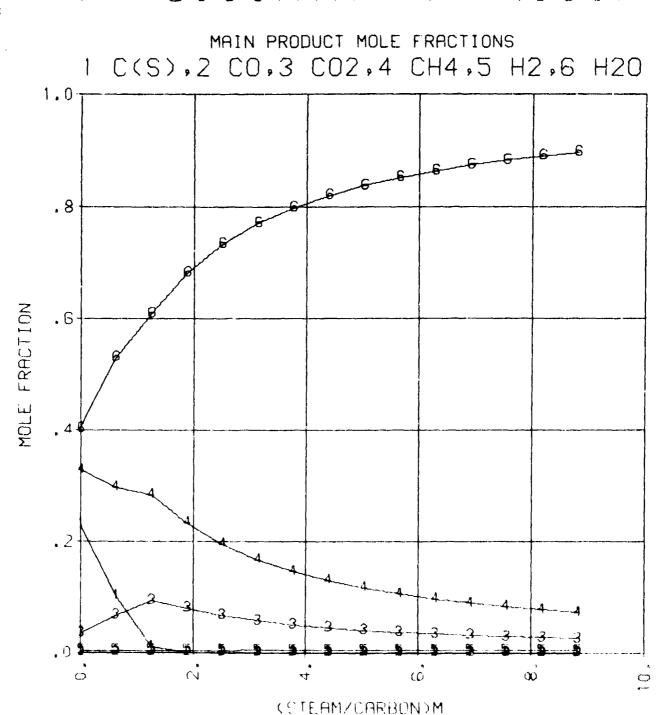


FIGURE 9.

STEAM REFORMING OF THE HYL FUEL P = 3.00 ATM

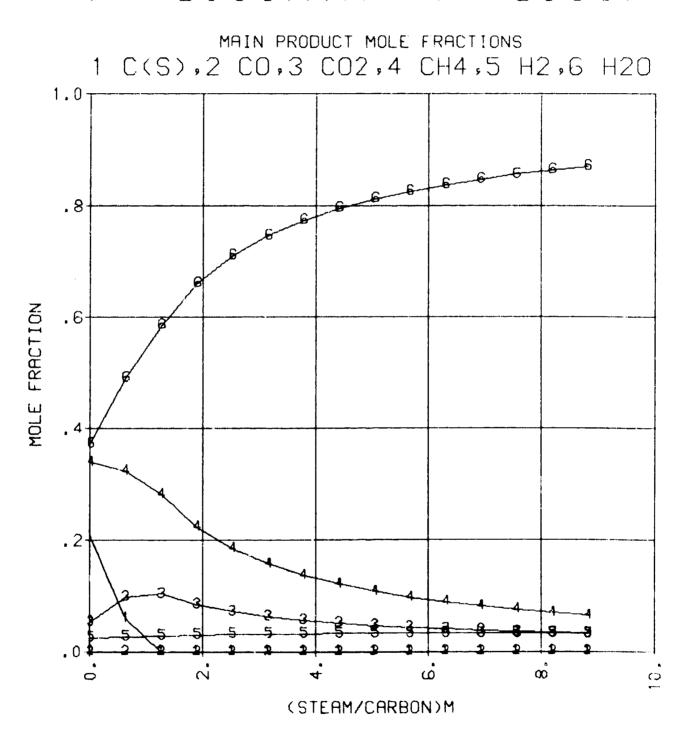
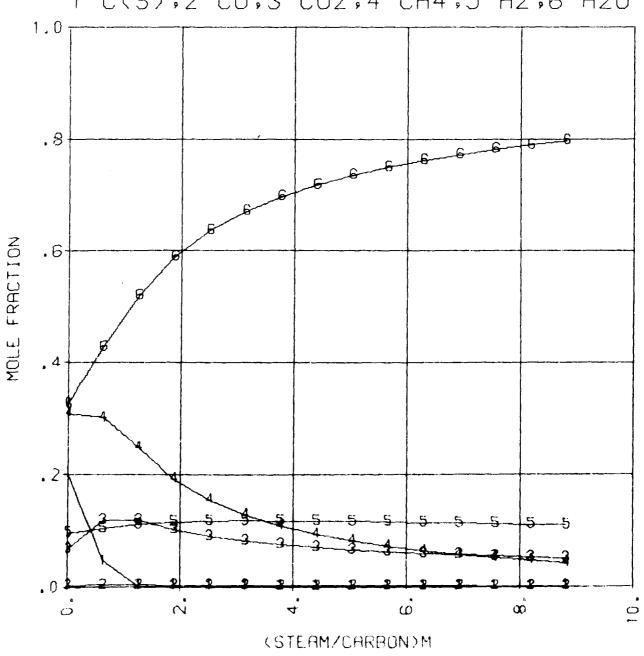


FIGURE 10.

STEAM REFORMING OF METHYL FUEL P= 3.00 ATM T= 800.F

MAIN PRODUCT MOLE FRACTIONS
1 C(S),2 CO,3 CO2,4 CH4,5 H2,6 H20



STEAM REFORMING OF METHYL FUEL P= 3.00 ATM T=1000.F

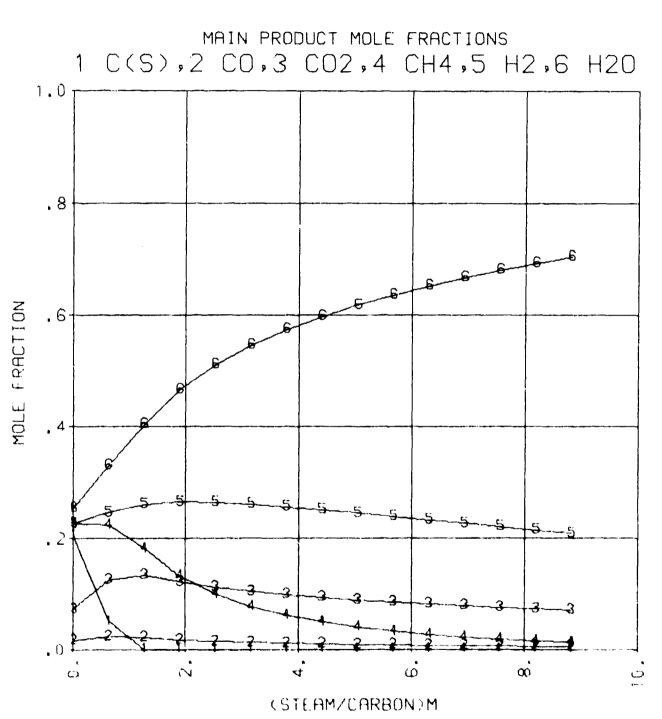
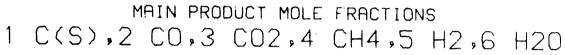


FIGURE 12.

STEAM REFORMING OF THE 1120 FUEL



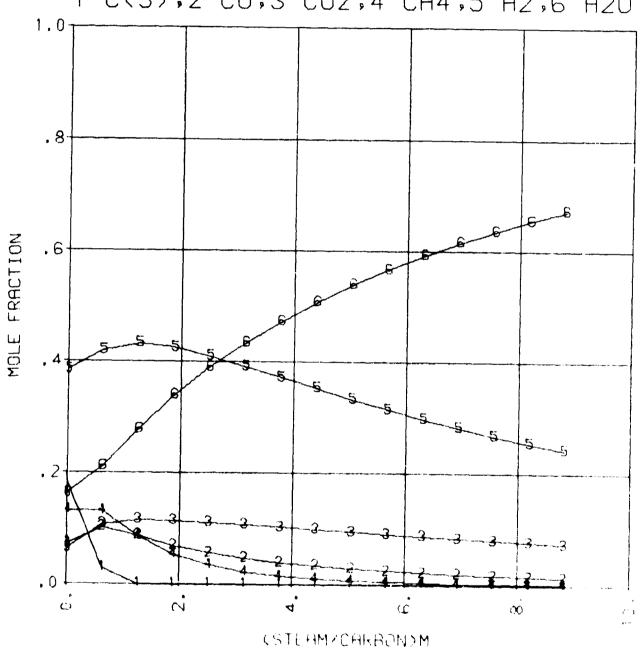


FIGURE 1 1

STEAM REFORMING OF METHYL FUEL P= 3.00ATM OF T= 1400.F

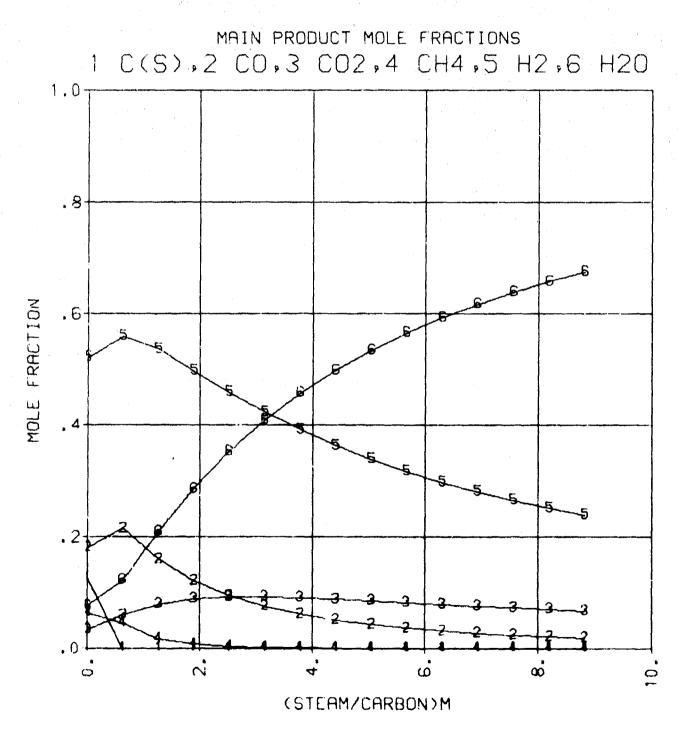


FIGURE 14.

STEAM REFORMING OF THE THYL FUEL PERSON OF THE THYL FUEL

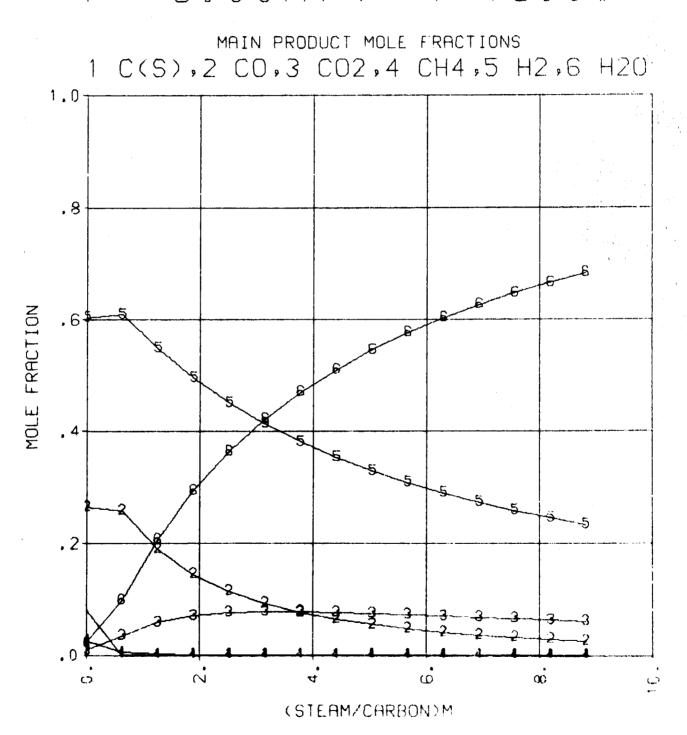
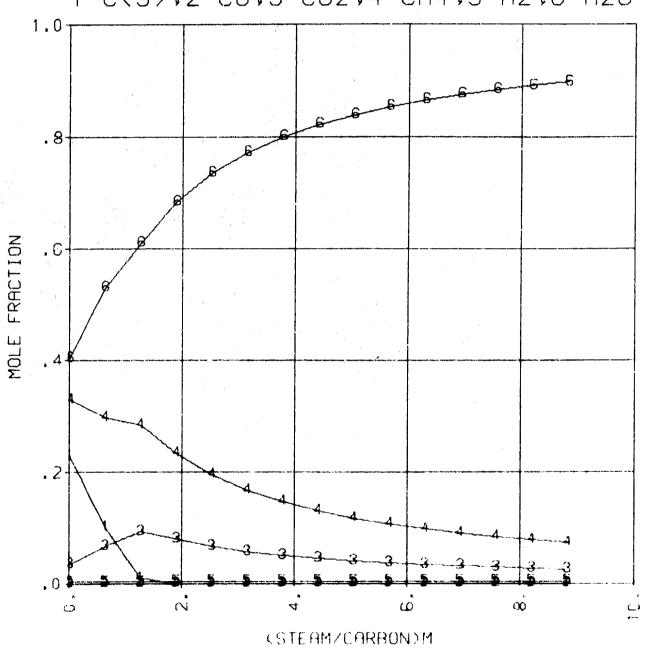


FIGURE 15.

STEAM REFORMING OF METHYL FUEL P= 5.00 ATM T= 400.F

MAIN PRODUCT MOLE FRACTIONS

1 C(S),2 CO,3 CO2,4 CH4,5 H2,6 H20



A-19

FIGURE 16.

PEAS. 50 ATM OF THE THYLOUTE

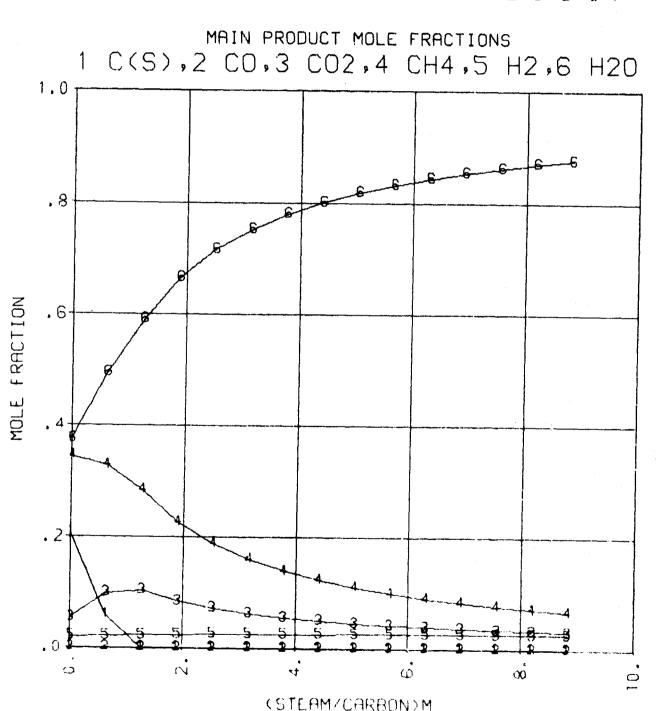


FIGURE 17.

PERS BRATING OF THE THY OF THE

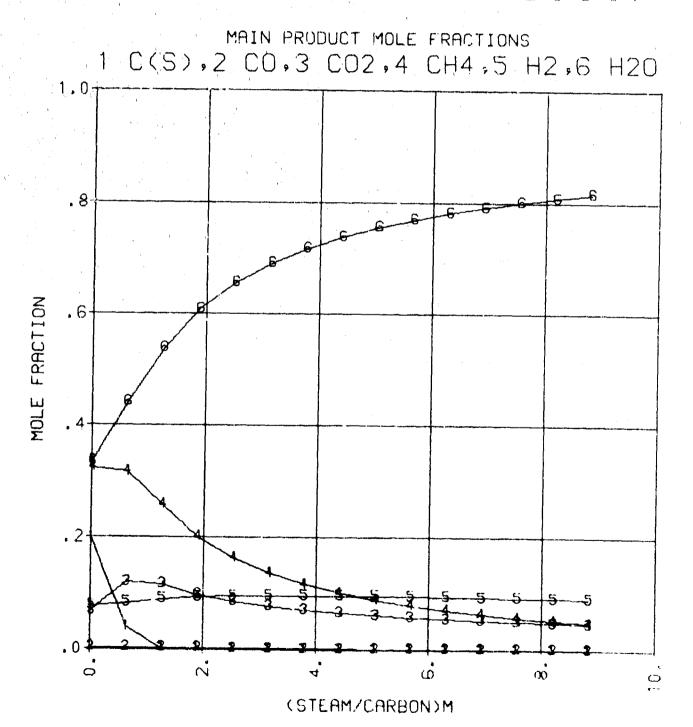
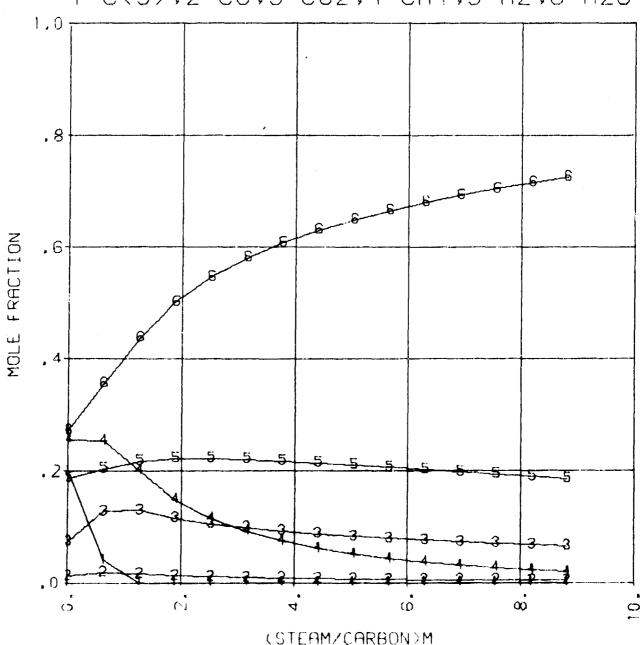


FIGURE 18.

STEAM REFORMING OF THE 1476 FUEL P = 5.00 ATM OF T = 100 6.F

MAIN PRODUCT MOLE FRACTIONS 1 C(S), 2 CO, 3 CO2, 4 CH4, 5 H2, 6 H2O



A-22

STEAM REFORMING OF METHYL FUEL PERSON TENED TO STEAM OF THE 1200 F

MAIN PRODUCT MOLE FRACTIONS

1 C(S),2 CO,3 CO2,4 CH4,5 H2,6 H20

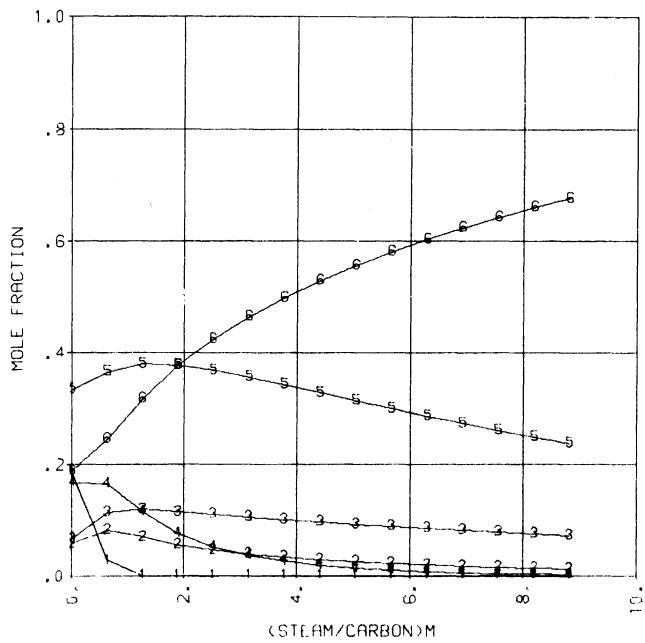


FIGURE 20.

STEAM REFORMING OF METHYL FUEL PERSON OF THE 1400 F

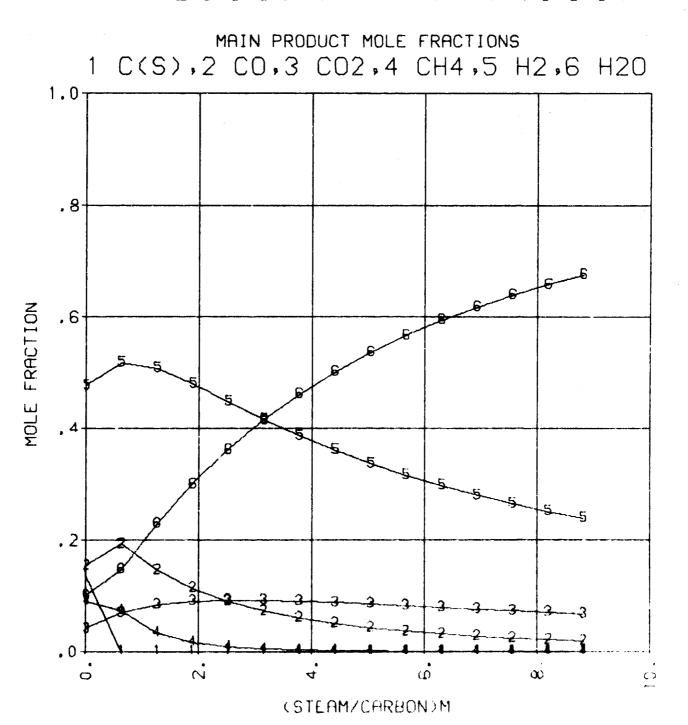


FIGURE 21.

STEAMS REFORMING OF THE 166 FUFT

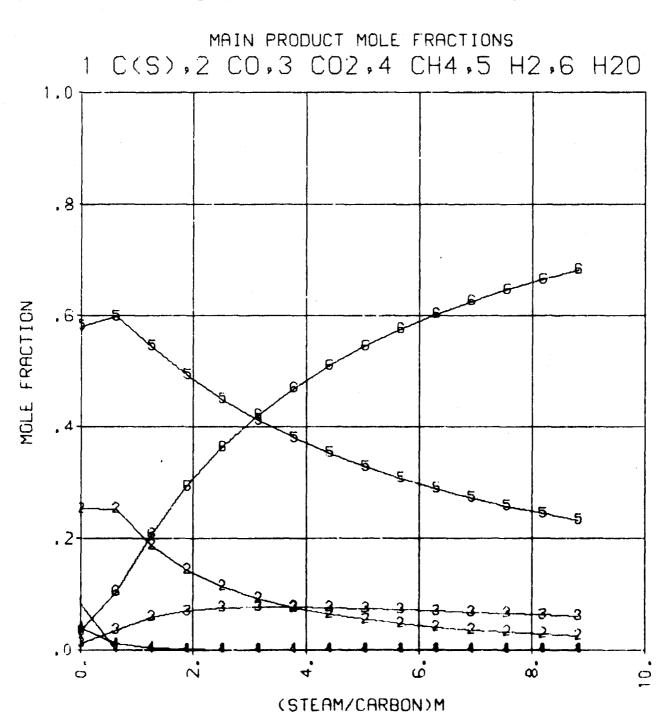
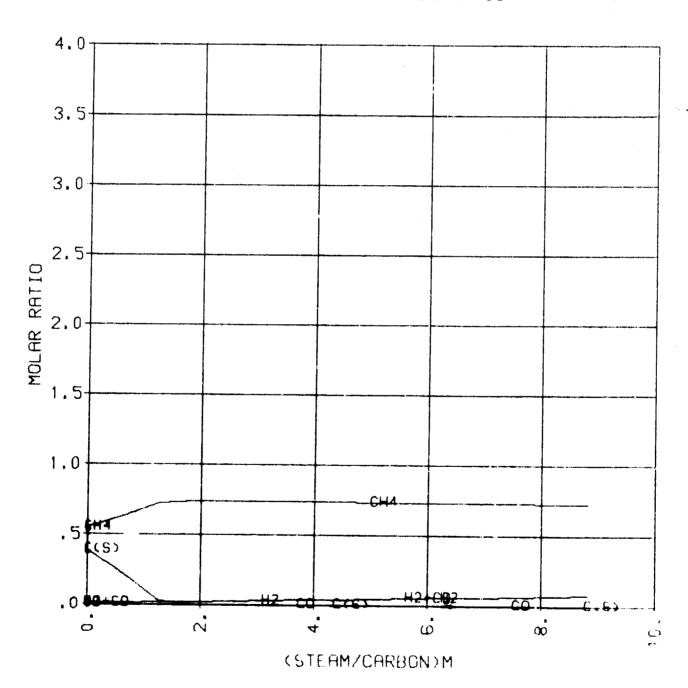


FIGURE 22.

STEAM REFORMING OF METHYL FUEL ON THE 400 F



A-26

FIGURE 23.

STEAM REFORMING OF THE THYL FUEL

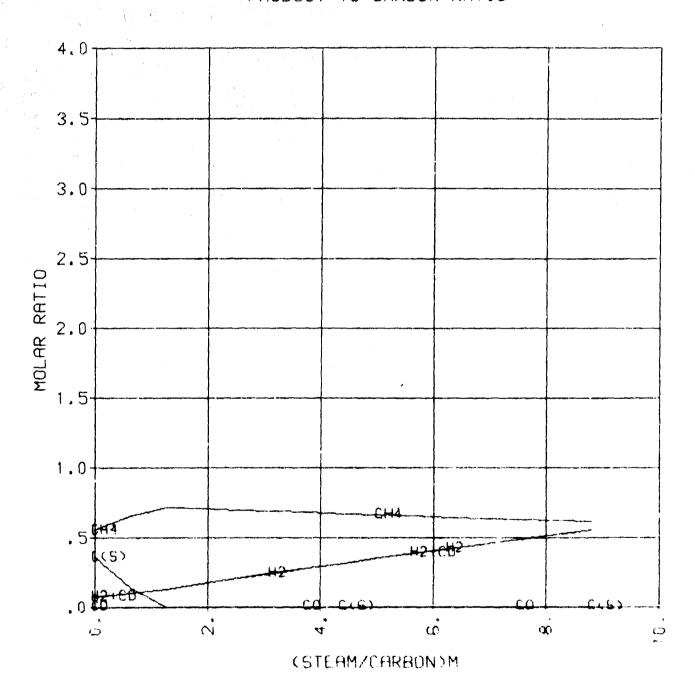


FIGURE 24.

STEAM REFORMING OF METHYL FUEL 800 F

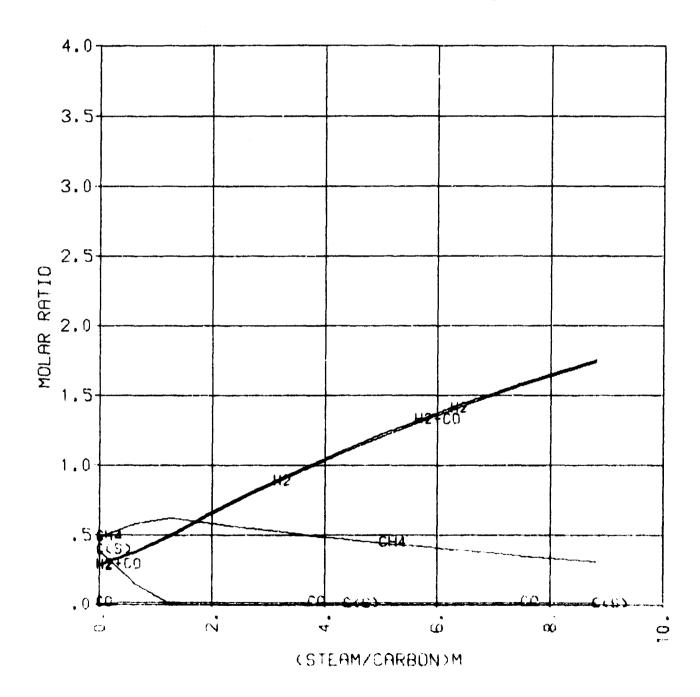


FIGURE 25.

STEAM REFORMING OF METHYL FUEL P= 1.000 FTM

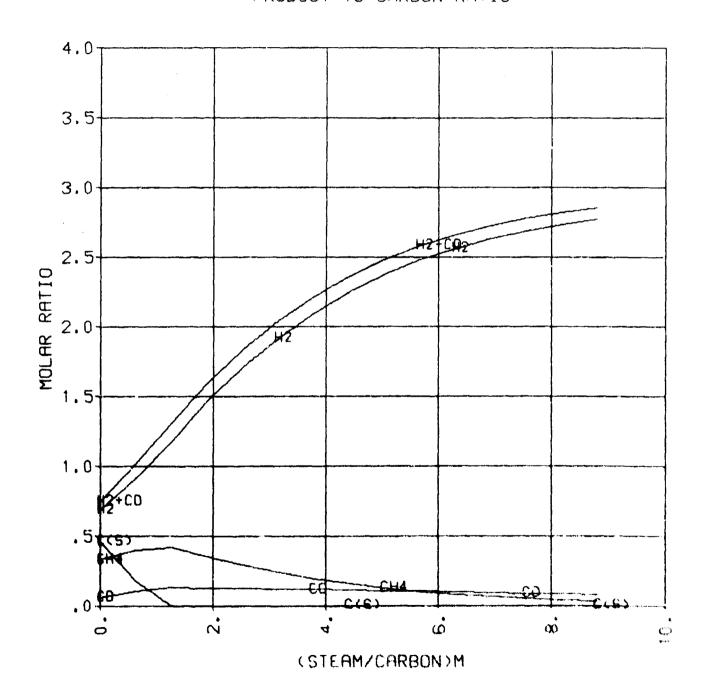


FIGURE 26.

STEAM REFORMING OF THE THYL FUEL P = 1 20 6 F

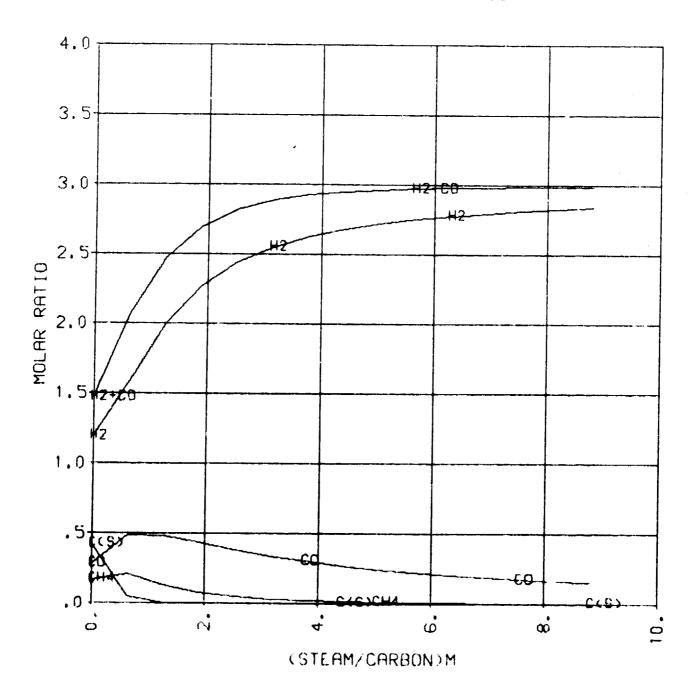


FIGURE 27.

STEAM REFORMING OF METHYL FUEL P= 1.00ATM T= 1400.F

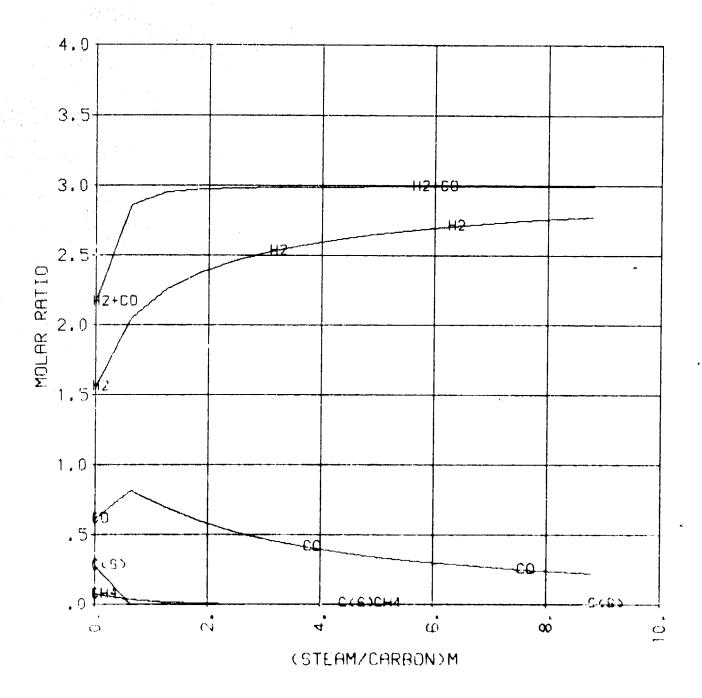


FIGURE 28.

STEAM REFORMING OF METHYL FUEL P = 1.00 ATM OF THE 160 FUEL

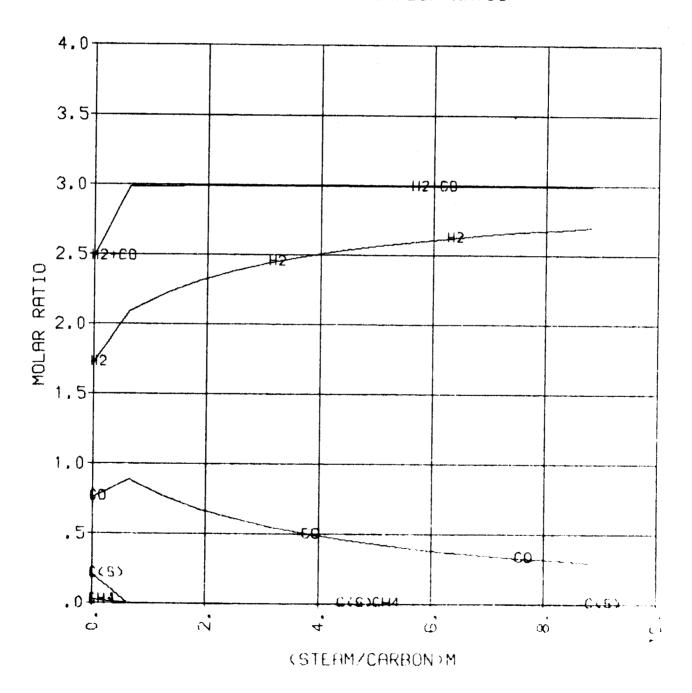


FIGURE 29.

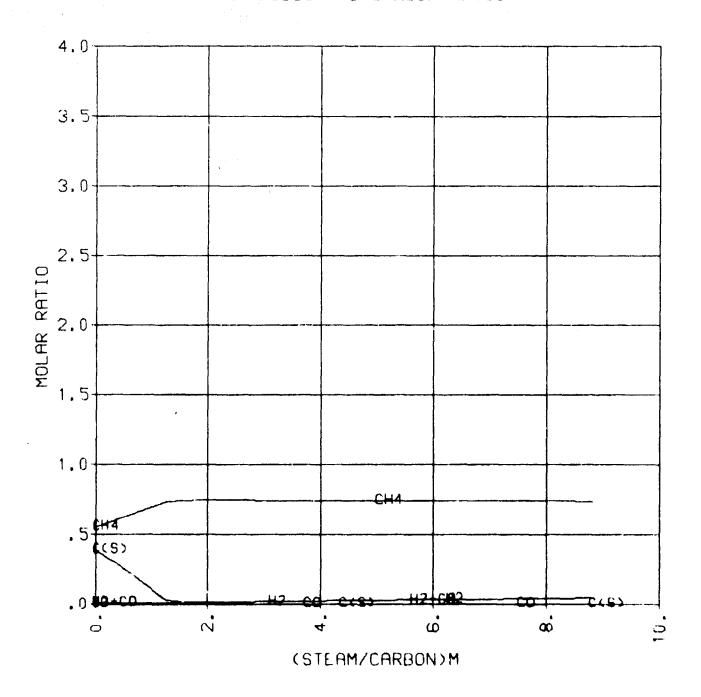


FIGURE 30.

STEAM REFORMING OF METHYL FUEL P= 3.00ATM OF TETHYL

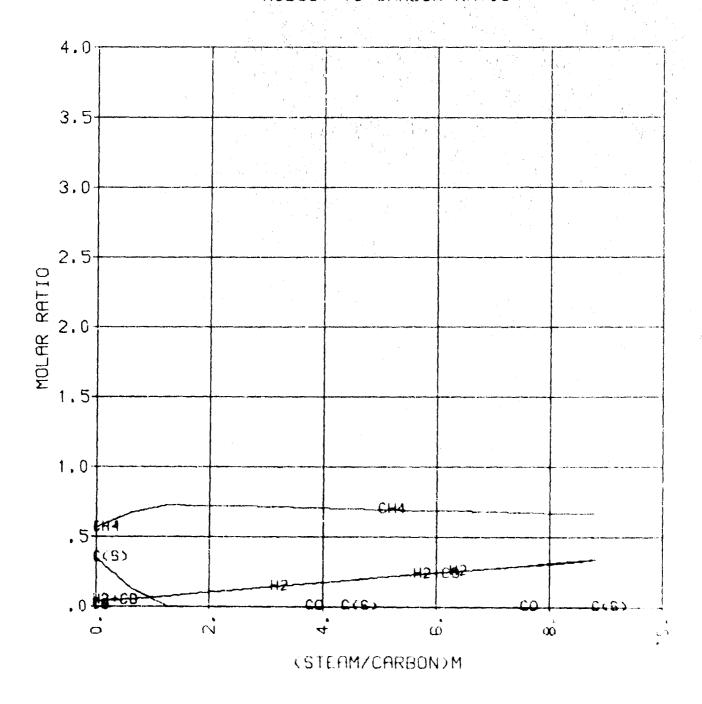


FIGURE 31.

STEAM REFORMING OF METHYL FUEL P= 3.00ATM OF TETHYL FUEL

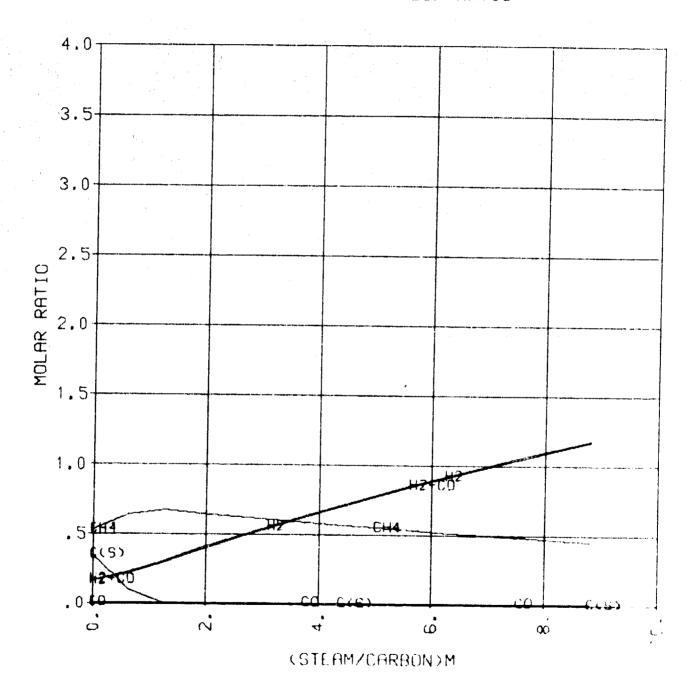


FIGURE 32.

STEAM REFORMING OF METHYL FUEL P= 3.00ATM OF T= 1000.F

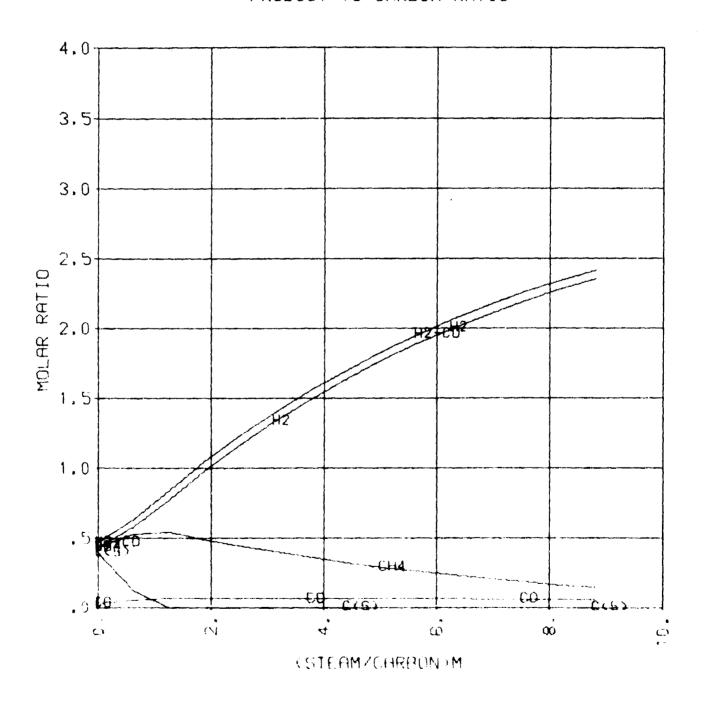


FIGURE 33.

STEAM REFORMING OF THE THYL FUEL P = 3.00 ATM

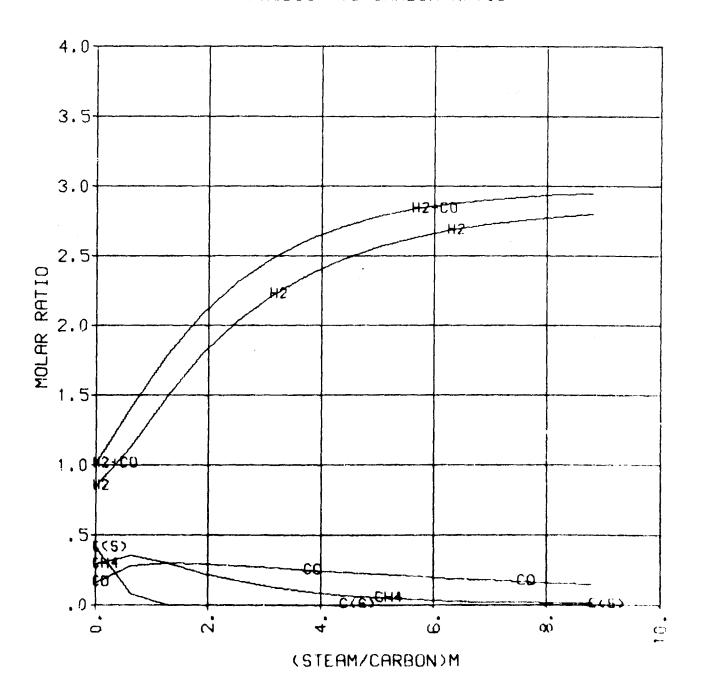


FIGURE 34.

STEAM REFORMING OF METHYL FUEL P= 3.00 ATM T= 1400. F

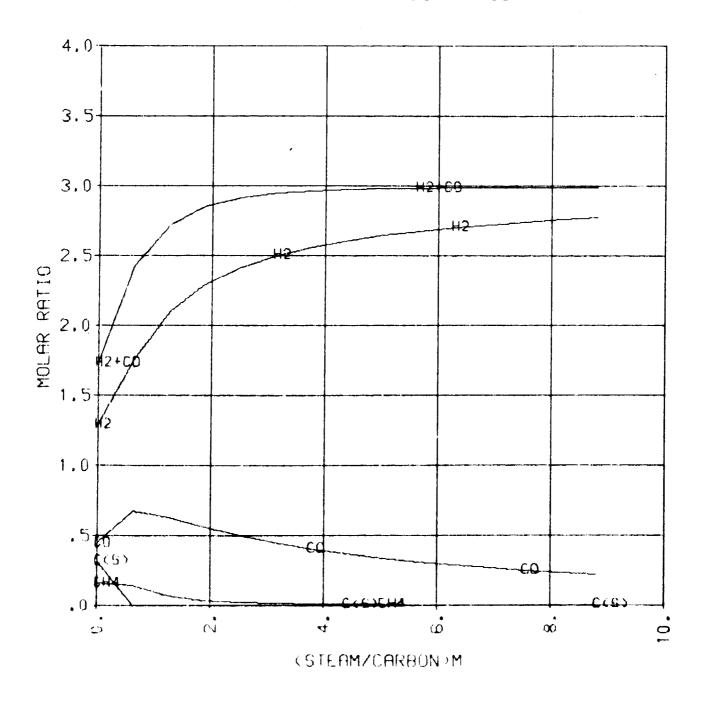
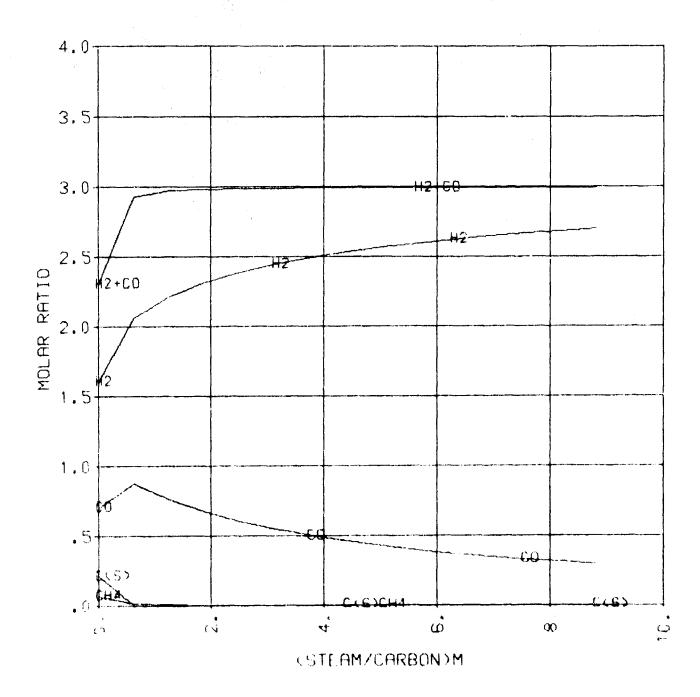


FIGURE 35.

STEAM REFORMING OF METHYL FUEL PERSON OF THE THYL FUEL



STEAM REFORMING OF METHYL FUEL P= 5.00ATM OF TETHYL FUEL

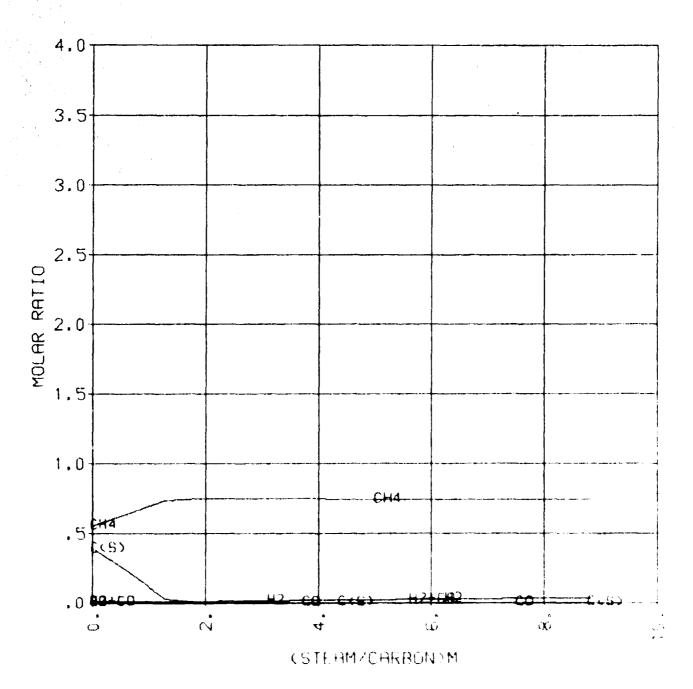


FIGURE 37.

STEAM REFORMING OF METHYL FUEL P = 5.00 ATM T = 600. F

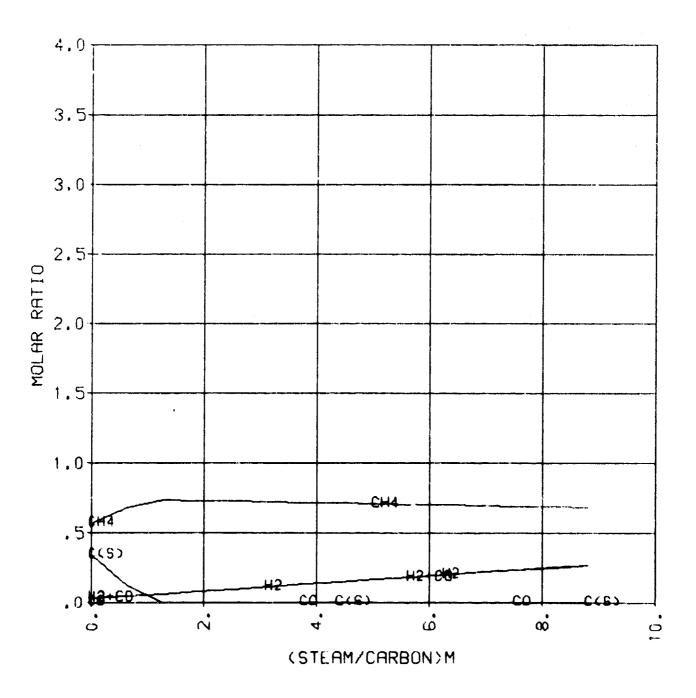


FIGURE 38.

STEAM REFORMING OF THE STATE OF THE

PROJECT IL CARBON RHIIL

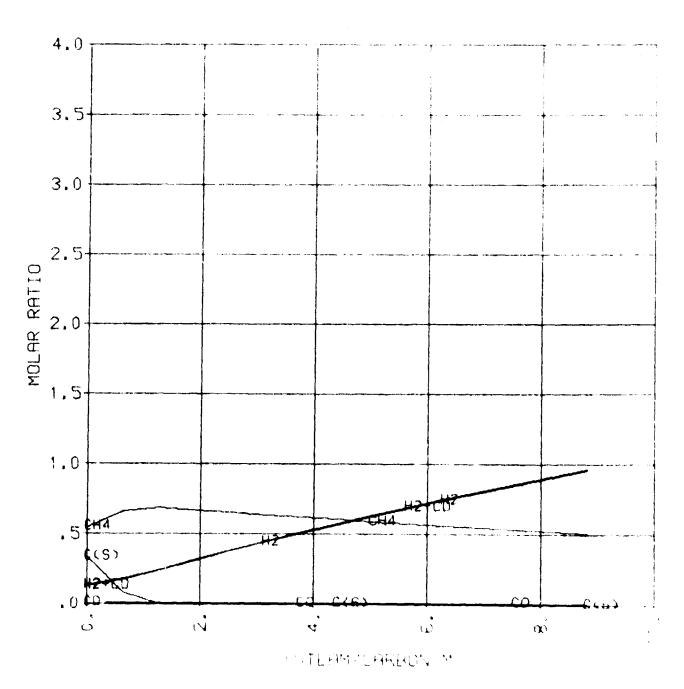


FIGURE 39.

STEAM REFORMING OF METHYL FUEL P= 5.00 ATM

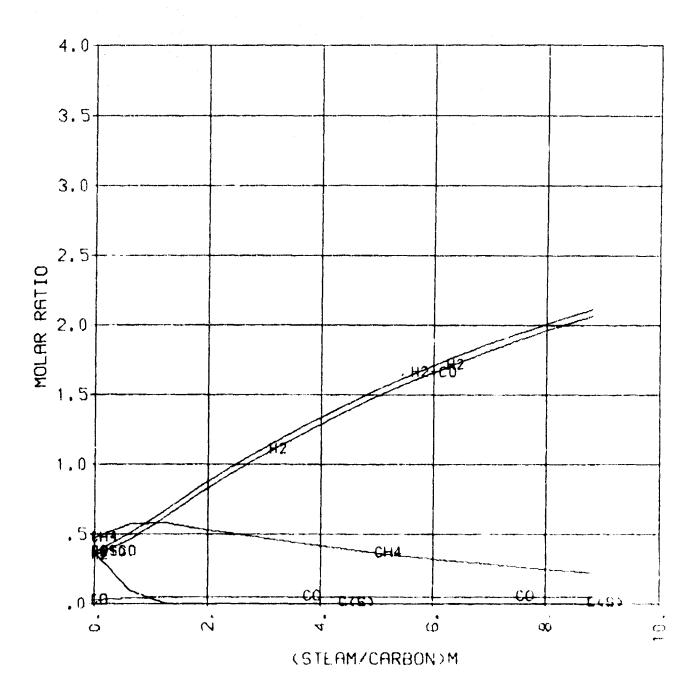


FIGURE 40.

STEAM REFORMING OF METHYL FUEL P= 5.00 ATM T= 1200.F

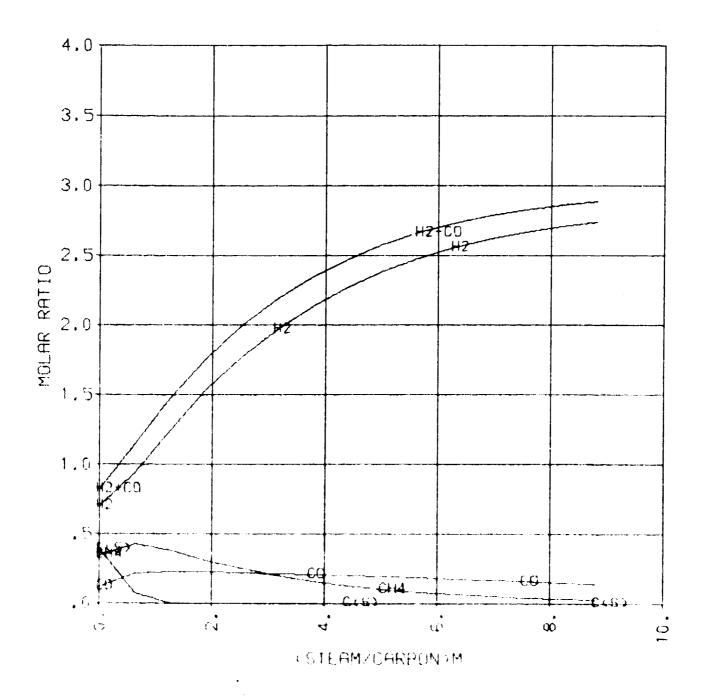
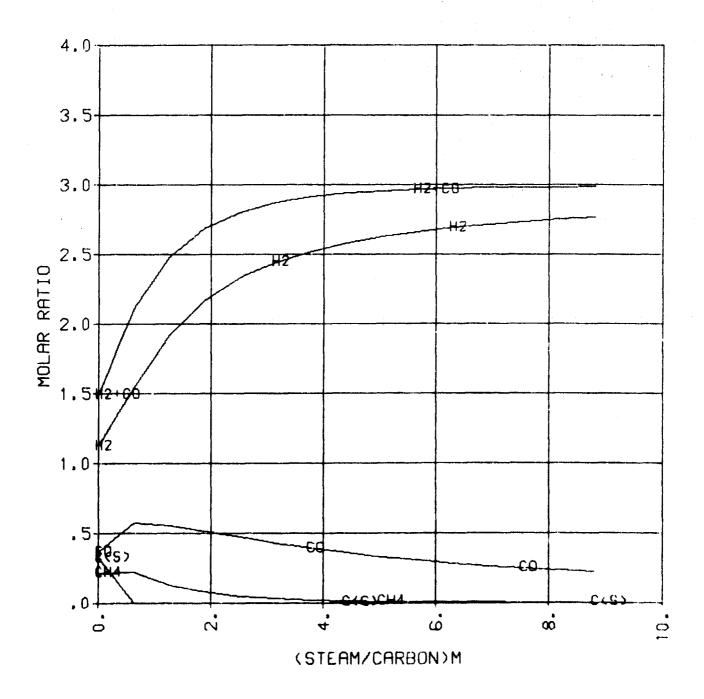


FIGURE 41.

STEAM REFORMING OF METHYL FUEL P= 5.00 ATM T= 1400 F



STEAM REFORMING OF THE THYL FUEL PERSON OF THE THYL FUEL

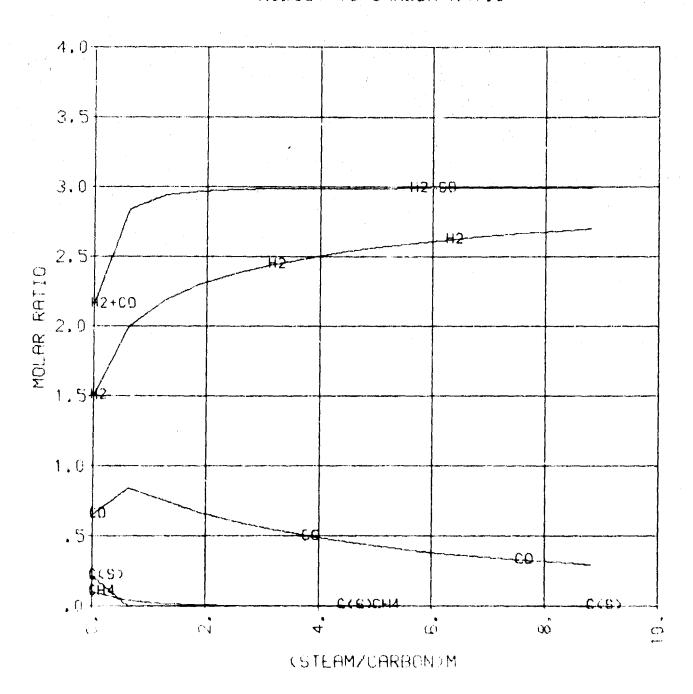


TABLE: 1 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #1.0: TEMPERATURE # 400.0F

H 20	.40563	.55138	14549.	.72029	.76844	.80209	.82693	.84603	.86117	.88366	.89956	.91140	• 92056	.92786	.93382
17	71900.	.00635	.00664	.00700	.00721	.00735	.00745	.00752	• 00757	.9200.	.00768	.00770	+00771	70	.00771
7 H J	.32476	.29070	.25837	.2023	.16600	•14069	.12201	99201.	.09628	.07939	.06746	.05859	.05172	.04626	.04181
202	.03611	.07454	.08928	.07048	.05835	98640.	.04360	.03879	.03497	.02931	.02530	.02231	.02031	.01816	99910.
00	.00000	00000•	00000	00000•	00000	.0000	00000	00000	00000	00000	.0000	000000	00000	00000	00000
(8)	.22735	.07702	00000•	00000•	• 00000	00000•	• 00000	• 00000	• 00000	• 00000	.0000	00000	00000•	00000	00000•
(H20/C) 4	0	.78722	1.57443	2,36164	3.14886	3.93608	4.72329	5.51050	6.29772	• 87	9.44658	11.02101	0	14,16987	15.74430
(H20/F1W	00•	•50	1.00	1.50	2.00	2.50	3.00	3.50	00.	5.00	00.9	7 • 30	8.00	60.6	10.00

TABLE: 2 MAIN PRODUCT COMPOSITION OF STEAM REFORMING HETHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #1.0: TEMPERATURE # 600.0F

Н2 0	.36817	610	. 60977	•	N	11092.	.78431	-0	17	2	566	884	784	.68429	927
12	.04324	-	.05023	.05231	.05332	.05379	.05395	-	.05380	.05334	.05273	.05207	.05137	.05067	86640.
* *	.32528	085	.24170	.18619	. 15054	.12572	.10746	934	.08242	.06608	• 05461	.04613	.03962	.03447	.03030
202	.05490	.10732	980	801	1890	0602	.05417	101	•04269	*00*0*	359	329	304	.02852	268
00	.00020	0	.00024	8	.00015	00	11000.	0	•0000•	.00008	.0000	90000	\$0000	• 00005	• 00005
(8)	.20822	.03610	00000•	• 00000	00000•	00000•	• 00000	• 00000	• 00000	.00000	.00000	• 00000	00000	$\overline{}$	00000•
(H20/C)H	00	.78722	7	_	•	3.93608	4.72329			7.87215	•	.021	95	.169	7
(H20/F)W	• 00	• 50	1.00	1.50	•	2.50	3.00	3.50	00·#	S • 00	•	7.00		00.6	10.00

TABLE: 3 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #1.0: TEMPERATURE # 800.0F

h20	.30291	60	5	7	155	6480	732		*0	375	585	758	908	03	.81472
Н2	.15249	99	~	80	199	0	•	.17227	0	623	.15560	490	426	.13641	304
CH4	.26360	571	917	139	073	850	689	.05681	47	0	249	186	40	107	82
C 0 2	,06796	276	208	.10508	943	964	803	.07541	71	647	595	553	.05176	486	8
00	.00361	S	*	.00350	2	25	22		.00179	70	.00129		600	00	.0007
C(S)	.20944	332	000	• 00000	000	000	• 00000	000	00	00	0	00	0	0	000
(H20/C1H	000	.78722	744	.361	3.14886	.936	23	• 510	6.29772	.872	• 4 4 6	.021	95	69	#
(H20/F)W		• 50		1.50	2.00	Š	3.00	S	4.00	0		7.00		00.6	

TABLE: 4 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE =1.0: TEMPERATURE =1000.0F

(HZ0/C)M	5)	0	2	\$	7	0
	121	282	7.16	5	238	085
	9	418	1294	\$	553	2787
	000	0328	353	107	989	531
	• 00000		1254	067	630	4167
		0223	.11710	043	.35090	465
	000	_	1098	~	359	990
	000	154	032	6	198	5417
	000	130	0972	13	034	5728
	00000•	.01113		.00924	.28727	009
	000	082	819	40	568	6484
	000	062	0735	02	301	6877
	000	048	1990	00	073	7201
	00000	038	605	00	880	7468
	000	031	0554	00	1717	69
	• 00000	•	_	00	1578	881

TABLE: 5 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #1.0: TEMPERATURE #1200.0F

Н2 Н20	.48654 .10778		.2450	.3767	e.	. 456	•	•	•	.26448 .64168	3273 .6	•	8737		
CH4	.06881	.06160	.02342	.00983	.00451	.00225	.00121	69000.	.00042	.00017	.00008	+0000.	.0000	10000.	
C02	.05300	.09335	.10734	.11042	.10824	.10371	.09833	.09284	.08756	.07809	.07014	.06351	• 05795	.05325	
00	.11580	.15918	.10919	.07774	.05720	.04342	.03391	.02714	.02218	.01558	.01153	.00887	.00703	17500.	
(8)	.16808	00000•	• 00000	00000	00000	• 00000	•00000	00000•	00000	00000•	00000	00000•	00000•	00000•	0 0 1 0
(H20/C)H	.00000	.78722		2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	.87	9.44658	11.02101	12.59544	14.16987	2000
(H20/F)W	00•	.50	1.00	1 • 50	2.00	2.50	3.00	3.50	00.	5.00	00•9	7.00	8 • 0 U	00.6	0

TABLE: 6 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #1.0: TEMPERATURE #1400.0F

# 2 0	7 .03	1 .1172	1 .2351	3 .32	74040	34. 6	7 .5153	45569	5920	208490	3069.	9 .7241	4 .7510	.7732	7918
H2	. 5885	66	3	476	.4267		-	~	~		-	203	~	167	*
CH4	.02642	* 9900 •	015	9000	.00024	.00012	•0000•	+0000•	0	10000	.00000	00000	00000	0	00000
202	~	0548	918	4060	917	9 6	864	826	.07872	713	8490	592	544	0503	467
0	.23299	.22187	67	.10335	•	.05883	466	378	.03132	224	169	131	105	9800	072
(5)	.09802	00000•	00000•	• 00000	• 00000	• 00000	90	00	00000	000	00	000	000	000	•00000
(H20/C)M	0	.78722	~	2.36164	3.14886	3.93608	32	5		=	S	210	754	9 6 9	15.74430
(H20/F)W	00•	• 50	1 • 00	1.50	2.00	2.50	3.00	3.50	00.4	5.00	00.9	7.00	9.00	00.6	10.00

TABLE: 7 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #1.0: TEMPERATURE #1600.0F

H20	.00779	1233	.24984	3453	.41959	788	272	.56745	~	6554	996	.72902	7.5	.77672	7947
1 7	291	467	Ŋ	409	4 1 1	.37241	.33962	• 31205	.28857	.25075	.22164	6-	.17982	9	.15125
\$ H U	10600.	.00036	.00008	.00003	.0000	10000	00000	00000	00000	00000	00000	00000	00000	00000	00000
C02	.00285	.04040	.06454	.07378	.07651	.07621	.07445	.07203	.06935	.06390	.05883	.05432	.05034	.04685	.04377
00	.28146	.23911	.16463	.12037	.09191	.07250	5867	9484	.04071	2991	2290	1810	1467		•1010•
(5)	69690.	00000•	• 00000	00000•	• 00000	• 00000	.00000	00000•	00000•	.00000	00000•	00000	00000	• 00000	.00000
(H20/C)H	0	.78722	1.57443	-	œ	3,93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	• 1 •	15.74430
(H20/F)W	00.	• 50	00•1	1.50	2.00	2 • 50	3.00	3.50	4.00	2.00	00•9	7.00	8.00	6 00	10.00

TABLE: 8 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE =3.0: TEMPERATURE = 400.0F

н 20	*	. 553	64.8	•7228	.7711	84.08		8489	. 8641	•	.9026	4160	. 9236	9016	.9369
Н2	•00326	.00368	.00385	0		4	0	.00438	4	4400	4	4	045	0.45	S
# HU .	.32674	92	2594	2032	10791.	9	62	19801	72	2	m	594	526	471	0426
C02	.03610	245	-	698	576	\$ \$	0428	0	4	285	7	.02155	192	174	158
8	• 00000	•00000	00000	.00000	00000	.00000	.00000	• 00000	.00000	00000	00	.00000	000	8	00
(8)	.22679	.07624	• 00000	• 00000	00000•	00000•	00000	00000•	• 00000	00000•	000	00000•	000	• 00000	
(H20/C)H	00000	w	1.57443	2.36164	7.	. 93	4.72329	5.51050	.29	.87	9.44658	11.02101	• 59	14.16987	15.74430
(H20/F) W	00.	• 50	1.00		2.00	2.50	3.00	3.50	4.00	2.00	00•9	•	8.00	9.00	10.00

TABLE: 9 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #3.0: TEMPERATURE # 600.0F

(H20/F)W	(H20/C)H	(5)	00	C02	4 KU	H 2	H20
• 00	00000	.20430	.0001	4	.33900	.02555	37
• 50	.78722	.03003	1000.	.10760	.32194	.02749	.51277
1.00	1.57443	• 00000	+1000.	.09397	.24945	.02994	62
1.50	2.36164	• 00000	•00010	.07565	.19361	.03135	.6992
2.00	3.14886	.00000	.0000	.06380	.15766	.03210	74
2.50	3,93608	00000	.0000	.05550	.13258	.03253	.77933
3.00	4.72329	00000•	90000	.04935	.11409	.03276	.8037
3.50	5.51050	• 00000	• 00005	.04462	16660.	.03288	.8225
00.	6.29772	00000•	•0000	.04085	.08868	.03292	8375
5.00	7.87215	• 00000	+0000•	.03523	.07205	.03286	.8598
00.9	9.44658	•00000	*0000°	.03123	.06033	.03270	.8757
7.00	11.02101	• 00000	.0000	.02823	.05163	.03247	.88763
8.00	•	00000•	.0000	.02589	.04493	.03222	.8968
00.6	14.16987	00000•	.0000	.02401	.03961	.03194	9
00.01	•	.0000	.0000	.02246	.03529	.03166	6

TM--04 MM 40--M

TABLE: 10 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #3.0: TEMPERATURE # 800.0F

(H20/F)W	(H20/C)M	(5)	8	202	4 H 2	H 2	H20
• 00	• 00000	.19781	.00211	.06856	.30728	·	.32850
• 50	.78722	.01422	032	129		201	4470
00•1	1.57443	• 00000	023	.10945	216	113	5.7
1.50	2.36164	• 00000	0018	092	1629	116	4254
2.00	3.14886	• 00000	.00151	081	1286		??
2.50	3.93608	• 00000	013	.07371	1049	117	.70271
3.00	4.72329	• 00000	.00114	.06771		1 1 6	40467
3.50	5.51050	00000	.00103	.06298	۱ ۰	5-	74611
00.7	6.29772	• 00000	.00093	.05913	.06410	1	.74147
2.00	7.87215	00000	• 0000 •	.05320	_	-	78547
00.4	9.44656	00000•	69000	.04877	.03858	108	
7.00	•	00000•	• 00062	.04528	_	105	*47.6
•	12.59544	• 00000	• 00055	.04244	.02530	102	6000
6 •00	٠	• 00000	05000	.04005	.02088	900	.81850
10.00	15.74430	• 00000	9+000•	.03799	.01739	.09705	.84712

TABLE: 11 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANGL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #3.0: TEMPERATURE #1000.0F

(H20/F)#	(H20/C)H	(5)	00	203	# H J	7	H20
00.	.00000	00	.01669	_	.22589	.22673	555
05.	.78722	199	Ö	1359	224	501	3
1.00	1.57443	00	33	1267	153	2633	371
1.50	~	000	0152	1139	901	940	900
2 • 00		0	012	ţ	11	260	15.4
2.50	3.93608	00	8		.05789	.25408	.57999
3.00	_	\sim	7	912	7	47	970
3.50	5105	• 00000	3	1980	3	39	=
*•00	2977	00000		817	26	,23217	518
2.00	8	000	0	42	•	16	960
9.00	4465	000	80	9690	20	0.2	7
7.00	0210	000	0040	0624	90	88	385
8.00	12.59544	00000•	0033	0577	40	.17488	595
00.6	869	000	28	535	02	62	77
00.01	15.74430	0	0024	0497	02	.15166	7941

TABLE: 12 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE =3.0: TEMPERATURE =1200.0F

H2 0	647	2511	3101	777	4334	4811	522	5595	5918	453	474	7209	7482	707	7895
15	, 38533	263	293	132	3906	3661	3	3187	974	2605	2307	065	1867	1702	.15644
\$ T	316	1302	189	0382	0222	0132	00	050	0032	9014	0007	000	0002	000	000
203	643	1149	1151	1116	1070	18	960	9160	989	0774	0698	633	0578	0531	0491
00	.07306	073	0771	0591	466	375	.03057	252	0210	5	0113	0087	690	950	-
C(S)	.18146	00	000	000	000	00	00	000	000	00000•	000	000	000	000	000
1420/C)H	000	72	.5744	5	. 1 488	.9360	~	5105	2977	721	4465	.0210	5954	.1698	3
(H20/F)W	00•	• 50	00•7	1.50	2.00	2.50	3.00	•	00·*	•	9.00	•	8.00	•	10.00

TABLE: 13 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #3.0: TEMPERATURE #1400.0F

H20	,07676	1442	2484	3261	4082	474	5165	5576	5025	6482	4907	7241	7510	730	~
7 1	.52110	5 9 5	172	479	. 42262	a 35	3501	3217	2973	2579	2275	2034	1839	1677	2
3 1	.06385	0348	113	4400	.00204	010	2000	0000	0002	000	000	0000	0000	0000	0000
C02	339	0652	842	116	0918	897	4980	0825	786		849	592	544	0503	467
00		-	387	00	075	582	463	3	312	.02243	168	.01316	105	980	072
(5)	.12228		000		000	• 00000	• 00000	000	• 00000	00000•	000	• 00000	0000	9	000
(H20/C)#	00	.7872	•5/44	2.36164	• 1488	9360	232	5105	.2977	7.87215	• 4465	.0210	24	• 1 698	~
(H20/F)W	00•	S	00•1	1.50	2.00	2.50	3.00	3.50	4.00	5.00	6.03	7.00	8.00	00.4	10.00

TABLE: 14 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #3.0: TEMPERATURE #1600.0F

H20	021	.25071	.	4789	273	54	6014	554	796	7290	551	.77672	7947
N I	603	.51975	9 =	372	339	312	8	50	21	9	79	4	151
4	0252	.00072	200	0000	000	000	000	000	000	0000	000	000	0
C02	770	90	0736 0745	762	* + 1	720	693	639	0588	543	50	891	.04377
00	267	*	1 7 O	072	50	40	0	.02990	22	8	.01467	12	.01019
(8)	• 07425	0000	000	• 00000	000	000	000	• 00000	000	000	• 00000	8	• 00000
(HZ0/C1H	007	1.57443	• & • &	90	7232	90	2977	8721	65	0	5	98	15.74430
(H20/F)W	00.	•	2.00	2.50	3.00	3.50	•	2 • 00	00.9	•	9.00	6	10.00

TABLE: 15 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #5.0: TEMPERATURE # 400.0F

(H2 ₀ /C)H	(51)	8	202	# # U	H2	H 20
0	.22662	00000	.03610	, 32735	.00276	. 40717
78722	009400	00000	.07452	.29308	.00285	•55355
57443	• 00000	00000	.08653	.25976	.00299	.64873
•	• 00000	00000	.06965	.20358	.00315	.72361
14886	00000•	00000	05747	.16733	• 00325	.77195
93608	00000•	• 30000	.04895	.14199	.00332	.80574
72329	00000•	•00000	.04267	.12329	.00337	.83068
51050	• 00000	•00000	.03784	10891	.00340	.84985
6.29772	00000•	• 00000	.03401	.09752	.00343	*86504
87215	00000	00000	,02832	.08061	.00347	.88760
44658	• 00000	.00000	.02430	.06866	•00349	.90355
4	00000	0	.02131	.05976	.00351	.91542
59544	00000•	.00000	00610.	528	.00352	.92460
9	• 00000	0	•01715	14240.	.00353	319
	• 00000	0	156	.04294	.00353	.93787

TABLE: 16 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #5.0: TEMPERATURE # 600.0F

H20	.37858	164	6318	705	54	85	.81011	828	439	62	82	894	.90323	9	67
H2	.01993	214	234	.02458	.02521	.02558	.02581	259	.02601	260	50	258	26	.02552	53
*H0	.34336	97	519	960	. 15997	348	.11627	020	0	+0+40+	0	0535	40	413	.03701
202	549	1076	9260	742	.06229	539	.04777	0430	.03925	336	0296	0266	T	224	020
0	•0000•	00	100	\sim	00	8	• 00005	000	+0000	000	.0000	000	000		
(8)	.20305	28	000	00	00	00	• 00000	0	00000	0	00000•	0	000	00	0
(H20/C1H	8	787	.574	.361	_	. 936	72	.5105	.2977	4	. 4465	.0210	.5954	1698	• 74
(H20/F)W	00•	• 50	00.1		•	2.50	3.00	•	• 00	•	00•9	7.00	•	9.00	•

TABLE: 17 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE #5.0: TEMPERATURE # 800.0F

H20	372	597	762	S	905	~	.74678	.76567	0	042	213	346	453	542	~
H2	~	37	=	*	960	53	.09495	43	.09353	17	97	11	57	38	5
\$ H O	22	9 1	25	7	136	12	4	*08095	70	3	4	36	29	25	21
C02	89	40	53	.08820	69	89	.06299	~	4	87	7	=	385	.03629	3 ₽ ₽
00	-	25	.00176	.00136	•00112	960000	• 000 •	920000	690000	0.5	15000	9	000		003
(8)	.19363	.00733	• 00000	• 00000	00000•	00000•	00000•	• 00000	• 00000	• 00000	00000•	• 00000	0		• 00000
1420/CJH	90	~	1.57443		~	Ö	_	5.51050	7	~	3	0210	595	.169	744
(H20/F)W	• 00	• 50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	2.00	00.9	7.00	8.00	9.00	10.00

TABLE: 18 MAIN PRODUCT COMPOSITION OF STEAM REFORMING HETHANDL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE =5.0: TEMPERATURE =1000.9F

H20	.27386	.37078	360	40.8	.61367	399	. 66165	+0089.	.71015	00t0/0	.75478	.77244	.78802	.80192
7	.18743	.20742	2222	2202	2165	2120	2079	018	1914	811	710	*19	523	36
\$ HO	.25534	.25410	1223	0916	0708	559	448	.03642	S	169	118	083	.00593	045
C02	.07535	∞ ~	1079	0982	9060	*	00	759	169	635	589	548	.05123	479
8	.01308	.01970	0113	944	.00813	071	90	57	40	039	033	02	.00251	02
(5)	10101.	.00921	0000	0	Ó	9	• 00000	.00000	• 00000	0	90	00	0	• 00000
(320/C)H	00	.78722	361	3.14886	936	723	105	6.29772	721	165	210	954	91.	3
(H20/F)W	• 00	1,00	1.50	2.00	2.50	3.00	3.50	00.	2.00	00.9	7.00	8.00	6 •00	10.00

TABLE: 19 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE =5.0: TEMPERATURE =1200.0F

(H20/F)W	(HZ0/C)H	(5)	ខ	200	¢HJ	Н2	H20
• 00	000	~	S	685	657	.33489	•
• 50	.78722	0	0853	1223	1633	713	25
1.00	.5744	00	0617	1171	0930	794	3486
	919	00000	0482	.11102	.05714		4130
•	1488	0	390	1051	364	557	635
2.50	36	0	032	9660	0238	385	5056
3.00	232	00	70	60	158	.32059	.54207
3.50	0	00000	~	895		O	741
4.00	977	00	194	849	72	856	6027
2.00	721	00	•01445	0765	035	S	6513
•	465	00	0110	69	018	272	404
7 • 90	.0210	000	086	0629	600	9	7229
9.00	12.59544	00000•	0	.05761	S	855	4
6 •00	.1698	000	950	530	003	69	714
10.00	7443	00	4	0440	002	559	7900

TABLE: 20 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE (90/10 WEIGHT RATIO)

PRESSURE =5.0: TEMPERATURE =1400.0F

H20	.10169	489		464	. 41430	4710	187	.55905	934	486	606	242	511	733	.79184
H2	.47729	178	. 49430	552	155	79	477	.32024	464	2574	272	033	1838	677	.15420
4 4	.09032	.06000	.02384	010	91500	.00270	.00151	.00089	• 00055	.00024	.00012	90000	+0000*	.0000	10000
202	.04208	39	75	N	.09203	•	.08628	.08247	.07859	.07125	62490	.05922	.05444	.05032	.04675
0	.15618	179	28	95	.07299	7	4	1	3.	22	9 -	13	0	.00863	.00720
(8)	.13243	• 60000	0	0	• 00000	• 00000	• 00000	00000•	• 00000	• 00000	00000•	• 00000	• 00000	• 00000	00000•
(H20/C)H	00	787	.574	.361	9	3.93608	723	5.51050	2977	8721	4465	210	13.4	• 1 69	15.74430
(H20/F)W	• 00	• 50	00•	•	2.00	2.50	3.00	3.50	00.*	2.00	00.9	7.00	8.00	6	10.00

TABLE: 21 MAIN PRODUCT COMPOSITION OF STEAM REFORMING METHANOL AND INDOLINE 190/10 WEIGHT RATIO)

PRESSURE #5.0; TEMPERATURE #1600.0F

H20	330	.13091	3464	201	7 7 2	5475	6014	•	9969	7290		4 4 4	947
H 2	823	.58507	4590	112	3193	3119	2884	2507	216	985	798	1643	1512
\$ HU	.03920	.00780	.00073	\$ £ 000 •	\$0000°	90000	.0000	• 00002	.0000			00000	_
C02	 :	.042/1	073	0 4	074	72	69	~	.05883	t D	503	468	.04377
0)	.25564	. 23352	(.07238	, C	.04843	69040.	.02990	229	.01810	146	121	•1010.
(8)	0778	20	00000	00000.	000000	• 00000	• 00000	\sim		• 00000	\circ	0	00000•
(H20/C) M	000	57	2 · 3 6 1 6 4	. 93	4.72329	2		.	3	11.02101	•	14.16987	15.74430
(H20/F)W	00.4	000	1.50	2.50	3.00	3.50	0 ·	2.00	00.0	00.7	00.0	4.00	10.00

TABLE: 22 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10790 BY WT)

PRESSURE =1.0: TEMPERATURE = 400.0F

TIELD TO CARBON RATIO

(H 2	650 .01045		75F10+ 614	.00000 .01912		71250			105*0. 00000.											
	.38650															00000			00000	
CH4/C1M CI	.55210	.65730	0 - 6 - 6	A 17 F	.74155	.73992	7 2031		1/96/1	.73512	73354	7777	,73039	.72727		./2417	.72109		• 7 1 804	171501
	00000•	.0000												.0000			10000		10000.	
(H2/C)H						.03216				•05137				• 68279						
(H20/C)H		.78722	1.57443		* 0 7 0 F 0 7	3.1.4886	3.93608	4.72320		05015.6	6.29772	7.072:0		859 * **	11.02101		14.54544	14.14007	\ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0	06++/-61
(H20/F)#		• 20	1.00	9		00·y	5. 50	3.00) (• • • • • • • • • • • • • • • • • • •	00.	20.00		00.0	7.00		00.0	00.0		

TABLE: 23 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT)

PRESSURE =1.0: TEMPERATURE = 600.0F

TIELD TO CARBON RATIO

(H20/F)W	(H20/C1H	(H2/C)M	H(3/03)	(CH4/C)M	0/(5))	(H2+C0)/C
00.	.00000		.00033	.55264	.35376	.07380
• 50	.78722		.0000	.68220	.07983	,10341
00•1	1.57443		.00072	.71086	.00000	14844
1.50	2.36164	.19631	.00070	.69871	00000	.19701
2.00	3.14886	.24332	69000.	.68696	00000	.24401
2.50	3.93608	.28902	690000	.67554		.28972
3.00	4.72329	.33358	.00070	.66440	00000	.33428
3.50	5.51050	.37710	.00070	,65351		.37781
00.	6.29772	99617.	.00071	.64287		. 42039
2.00	7.87215	.50223	.00072	,62223	.00000	.50295
••00	9.44658		.0007	.60237		.58238
7.00	11.02101	.65823	• 00075	.58322	.00000	.65899
8.00	12.59544		.00077	.56472		.73301
00.6	14.16987	•	.00078	.54681	00000	.80464
10.00	15.74430		.00080	.52946	• 00000	+0+28.

TABLE: 24 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10790 BY WT)

PRESSURE #1.0: TEMPERATURE # 800.0F

YIELD TO CARBON RATIO

(H20/F)W	(H20/C)H	(H2/C)H	H()/0)	1CH4/C)M C(S)/C		(H2+C0)/C
00•	•00000		.00662	. 48403	~	.28662
• 20	.78722			.60715	07856	91904.
1.00	1.57443	.55879		. 60475		.57287
1.50	2.36164			.56310		• 73945
2.00	3.14886	.87935	.01421	.52458		89355
2.50	3.93608	-	.01439	.48865		1.03729
3.00	4.72329			.45498		1.17196
3.50	5.51050	1.28377		. 42335		1.29846
00.	6.29772		.01483	.39358		1.41754
5 •00	7.87215			.33915		1.63525
00.9	9.44658		.01501	.29091	00000	1.82821
7.00	11.02101		.01492	.24830		1.99865
8.00	12.59544		.01472	.21087	00000	2.14840
6 • 00	14.16987		• 01445	.17821	00000	2.27903
10.00	15.74430	2.37797	.01411	14995	00000	2.39208

TABLE: 25 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT)

PRESSURE #1.0: TEMPERATURE #1000.0F

YIELD TO CARBON RATIO

(H2+C0)/C	.75269	1.08584	1.45348	1.77468	2.03821	2.25229	2.42352	2.55807	2.66197	2.80057	2.87845	2.9222	2.94740	2,96239	2.97166
0/(5)/	. 45355	.11079	00000	00000	.00000	. 00000	• 00000			00000•	• 00000	.00000	00000		
(CH4/C)#	.33302	.42111	.38460	.30430	,23841	.18489	.14209	.10845	.08247	.04782	.02835	.01741	.01112	.00737	.00505
H(3/03)	.06032	.11440	.12885	.12593	.12217	.11738	.11177	.10563	.09929	.08695	.07603	.06688	.05937	.05320	.04811
(H2/C)H	.69237	99144	1.32463	1.64875	1.91604	2-13491	2.31176	2.45244	2.56269	2.71362	2.80242	2 • 85533	2.88803	2.90919	2.92355
(H20/C)H	00000	.78722	1.57443	2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F)W	00•	• 50	1.00	1.50	2.00	2.50	3.00	3.50	00.	5.00	9.00	7.00	8.00	9.00	10.00

TABLE: 26 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT)

PRESSURE #1.0: TEMPERATURE #1206.0F

YIELD TO CARBON RATIO

M10/0/H2	11.0/CH	***************************************	***************************************		
E ,	E / 7 / 7	こっくつく	ヒーンシナエノー	7/617	3/(03+24)
000	1.19934	.28544	.16962	1641431	1.48477
1722	1.70074	.50673	.19610		2.20748
1.57443	2.14635	. 45504	.09762		2.60139
2.36164	2.40056	.39266	99640*	•	2.79322
3.14886	2.54916	, 33655	.02654	•	2.88571
8098	2.64097	.29066	•0120		2.93163
1329	2 • 70155	.25409	906000	•	2.95564
5.51050	2 - 7 4 4 0 3	.22491	.00573	•	2.96894
6.29772	2.77536		.00379		2.97671
7.87215	2.81849	•	.00184	•	2.98450
9.44658	2:84689	.14099	.00100	•	2.98788
2101	2.86710	•	• 00059		2.98952
12.59544	2.88226	.10814	.00037	00000	2.99040
14.16987	2.89408	•	.00024		2.99090
1430	2.90357	.08764	.00016	00000	2.99121

TABLE: 27 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE #1.0: TEMPERATURE #1400.0F

YIELD TO CARBON RATIO

77.0346H1 37.813	7/107/7/17			0 0 7 0 7		2.98053							2.99104							2.901A1		
271817	24107					00000•			00000				00000							• 00000		
# CUAHU	.07037		.02343	47400		.00283	.00142		· .000 •	.00048	15000		.00021			90000.	.00003		.0000	.0000		10000
M(3/03)	.62057		.78296	63833			. 45397									.20673	. 18191		.16223	9 1 4 6 4 6	1300	~ トつつ ・
(H2/C)H	1.56765			2.32648			2.53222	7.50214		2.63978	2 • 67 6 6 2	1 (1	2.70648	2.75.193		2.78491			16479.7	2.84535	2.05015	170004
(H20/C)M	.00000	(() ()	77/0/	1.57443	2.3414	10105.1	3 • 1 4886	3.03608		426710	5.51050	100	21112	7.87215		95070	10120-11	12.105.44		14.16987	15.74420	
(H20/F)W	00•	C 14	00	00•	1000		2.00	2.50		00.5	3.50			S•00	•		00.			00.	10.00	

SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT) TABLE: 28

PRESSURE #1.0: TEMPERATURE #1600.0F

TIELD TO CARBON RATIO

(H2+C0)/C	2.50803	2.98473		++064.7	2.99125	2.99155		20164.7	2.99175	2.90170		2.99181	7.00164	101119	2.99185	70.00	C0 1 6 1 0 7	2.99186		2.99186	2.99186
))/(5))	• 19195	00000			• 00000	00000			00000•	00000		00000•	00000		00000•	רייטטיי		• 00000		00000.	• 00000
H(CH4/C)H	.02498	• 00158	J000		\$1000.	•0000•	20000		50000	• 00002	0 0	10000	• 00001		00000	00000) : () (• 00000		00000	• 00000
H()/0)	.77521	.85437	.71813		20 -	99545.	. 48753	44040	7/6/1	. 40219	26026	04.00	.31882	0.000	A 1 00 7 4	*54664		096771	.20540	9 6	98661.
(H2/C)H	10/3/02	cc251.7	2.27232	2.17.17		10541.7	2.50415	2.55.03		0968517	2.62191		708/907	2.71146		74 1 4 7 9 7	70,110	0900/1	2.78427	2.0000	10500.7
H20/C)H	7872	77	2447501	2,36164	3.1480.	990111	800000	4.72329	5.0100		6.29772	7.972.5		4 - 4 - 6 5 8	11.00.01	7011711	12.59544		18401011	15.74420	
(H20/F)W	• 50		•	1.50	2.00	2.50		20.5	3.50		00.*	5.00		00.0	7.00)	8.00	0	000	10.00	

TABLE: 29 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT)

PRESSURE =3.0: TEMPERATURE = 400.0F

TIELD TO CARBON RATIO

77 C T C M T	7 1														759700 000					0,440. 000
2/18/2				00000•				00000		00000			00000			00000*				00000
MCD/HD)	.55414	45.000	, o, c,	0747.	.74425	. 74330	74334	977.	.74143	.74050	72057	\n\n\n\n	. 73772	.73588		0010.	.73223	73042	7.05.4	.72862
H(3/03)	00000	10000		10000	• 00001	0000			.0000	10000	ייטטטיי	1000	• 00001	.0000			.0000	10000	1000	• 00001
(H2/C)H	*0900	.00830	901104		.01487	•01865	.02241		*1920*	.02987	.03258		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	.04833	.055.65		• 06293	.07n18		0 1 2 4 0
(H20/C)H	• 00000	.78722	1.57443		4 9 3 0 1 6 4	3.14886	3.93608	10,10	4757/or	5.51050	6.29772	7.07215		4.44658	11.02101		14.51544	14.16987	1000	071710
1420/F1W	00.	• 50	1.00		2001	2 • 00	2.50			3.50	00.	7		00.4	7.00	•	00.0	00.6	C .	00.

TABLE: 30 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT)

PRESSURE =3.0: TEMPERATURE = 600.0F

YIELD TO CARBON RATIO

(H2+C01/C	.04289	.04017	00756	44411	14578	17326	20075	.22780	77444	80906.	15724	40682	45.51	46003	.54851
0/(8)/0	4	.06532			00000	00000	00000	00000		00000		00000			00000
CH4/C)#	.56653	.70026	.72408	71878	.71165	.70465	.69778	.69102	68436	67132	65863	.64626	63418	62238	.61084
M(3/03)	•1000	•00038	04000	.00038	.00037	.00037	.00037	.00037	.0003B	•00038	• 000	.00039	04000	04000	.00041
(H2/C)H	.04270	•05979	.08715	•11638	16441.	.17288	.20037	.22742	• 25406	.30620	.35695	. 40643	.45473	.50193	.54810
(H20/C)#	00000	.78722	1.57443	2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F1W	00•	• 50	1.00	1.50	2.00	2.50	3.00	3.50	* 00	5 • 00	00.9	7.00	8.00	00.6	10.00

TABLE: 31 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE =3.0: TEMPERATURE = 800.0F

TIELD TO CARBON RATIO

C(S)/C (H2+C0)/C	. 75	01.4014 000.00	003174 .24163				.00000				.00000 .84137			.00000 1.08852			*00000 1 *37909	1,5000		.00000 1.63218	-
CH4/C)M CIS) •				7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	107501	. 60733	.58307				-51424						.37047		. 33992	.31141
H(3/03)	400344		• 00717	-00715	90700		.00713	.00721		77.00.	.00742	.00752		.0071	.00787		00000	01800		.00617	.00822
(H2/C)H	• 16630		• 23446	.34568	45.254		.55542	•65238	74507		.83395	. 91937		1 = 0 9 0 = 1	1.23101	-	007/507	1.50187	. 0	104701	1.73803
(H20/C)M	• 00000		27010	1.57443	2.36164		3.14886	3.93608	4.72320		9.51050	6.29772	7 073:0	517/90/	9.4465E	11.0210.	70140	12.59544	- 00Y . 71	/9401011	15.74430
(H20/F)W	00•	0	000	• 00	1.50		00.2	2.50	3.00) (3.50	**	000	00.0	9 •00	7.00		00.8	0,0		00.01

TABLE: 32 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE #3.0; TEMPERATURE #1000.0F

TIELD TO CARBON RATIO

(H2+C0)/C	47020	7.1043		847440	1.18633	1.40252	1.59636	1.77034	1.02420	0707/17	4.000.0	0144707	144/407	2.61662	2.71761	2.79099	2.84377
))/(5))	60	0.4012		00000	• 00000	00000	00000	00000					00000	00000	00000	00000	00000
M (D/ HU)	. 43633	55.355	51197	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	. 45, 38	46796	.34888	.30538	.24640	23157	17317	10101	///710	19860.	•06856	.05022	.03702
H(3/03)	.03225	.06179	0.440		4/400	•06504	.06513	+649U·	.06445	06368	1900	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	71000	66440.	.05141	.04787	.04450
(H2/C)H	•43796	.61762	.87928	73.61.1	0017101	1.33748	1.53123	1.70540	1.86182	2.00191	2.23776	2.42157		60100.7	2.66620	2.74312	2.79927
(H20/C1H	• 00000	.78722	1.57443	2.36144	F010511	3 . 1 4886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02.01		14.54544	14.16987	15.74430
(H20/F)W	00•	• 50	00•1	0.5) (2.00	2.50	3.00	3.50	*•00	8. 00	9 00	7.00		00.0	6	10.00

TABLE: 33 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL(10/90 BY WT)

PRESSURE #3.0; TEMPERATURE #1200.0F

TIELD TO CARBON RATIO

(H2+C0)/C	1.01762	1.51379	1.94463	2.25978	2.48607	2.64442	2 • 7 5 2 7 3	2.82578	2.87488	2.93073	2.95756	2.97135	2.97891	2.98331	2.98600
) 3/(8))	. 40284	.00000	00000	00000	00000	• 00000	00000	00000	.00000	00000	.00000	00000	00000	00000	00000
H(CH4/C)H	.29214	39495	.26181	.18302	.12645	.08686	.05979	.04152	.02925	.01528	.00858	.00513	,00324	.00214	.00147
H(3/03)	_	.30436	.29617	.28283	.26535	.24579	.22598	.20715	.18993	86091°	.13856	.12115	.10743	.09640	.08737
(H2/C)H	.85542	1.20943	1.64846	1.97694	2.22072		2.52674			2.76975	2.81901	2.85019	2.87148	2.88691	2.89863
(H20/C)H	• 00000	.78722	1.57443	2.36164	3.14886	3.93508	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F)#	00•	• 50	1.00	1 • 50	2.00	2.50	3.00	3.50	00 • ¥	2.00	00.9	7.00	8.00	00.6	10.00

TABLE: 34 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10790 BY WT)

PRESSURE #3.0: TEMPERATURE #1400.0F

YIELD TO CARBON RATIO

H2+C01/C	1.74861	2.52576	2.79856	2.90040	2.94367	2.96423	2.97493	2.98092	2.98449	2.98616	2.98980	2.99063	2.99108	2.99134	2.99150
C(5)/C (H2+C0)/C	.30408	00000	00000	00000	.00000	00000	.00000	00000	00000	00000	• 00000	00000.	• 00000	• 00000	00000
CH4/C)M	.15878	.11653	.04833	.02287	.01205	.00691	.00423	.00274	.00184	.00093	.00052	.00031	.00020	.00013	•0000•
H(0/0)	.45280	•66536	.59207	.51198	44446	.39074	.34751	.31245	.28359	.23910	.20652	.18170	.16217	.14642	.13345
(H2/C)H	1.29581	1 • 8 6 0 3 9	2.20649	2.38842	2.49899	2.57349	2.62742	2.66847	2.70089	2.74906	2.78328	2 • 80893	2.82890	2.84492	2.85806
(H20/C)H	00000	.78722	1.57443	2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F1K	• 00	• 50	1.00	1 • 50	2.00	2.50	3.00	3.50	00°	2.00	9 • 0 0	7.00	8.00	9.00	10.00

TABLE: 35 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE #3.0: TEMPERATURE #1600.0F

VIELD TO CARBON RATIO

(H20/F) W	(H20/C)H	[H2/C]H	H(3/03)	M(D/AHD)	2/(5)/	(H2+C01/C
• 00	.00000	1.61248		.06728	.19824	2.32626
• 50	.78722	2.10568		.01092	00000	2.94820
00•1	1.57443	2.26432	.71496	.00315	00000	2.97928
1.50	2.36164			.00137	00000	2.98639
2.60	3.14886	2.44396	.54505	.00071	00000	2.98902
2.50	3.93608			.00041	00000	2.99022
3.00	4.72329	2.55031	•	.00026	00000	2.99084
3.50	5.51050			. 00017	00000	2.99119
00.	6.29772		.36983	.00012	00000	2.99140
2.00	7.87215			90000	00000	2.99162
••00	9.44658	2.71156		.00003	00000	2.99173
7.00	11.02101			.00002	.00000	2.99178
00.0	12.59544			.0000	00000	2.99181
6. 00	14.16987	2.78624		.00001	00000	2.90183
10.00	15.74430		. 18885	.0000	00000	2,99184

TABLE: 36 SURVEY THE STEAM REFORMING OF INDOLINE AND HETHANDL (10/90 BY WT)

PRESSURE =5.0: TEMPERATURE = 400.0F

YIELD TO CARBON RATIO

		11.000	M. 7.07	M () / #H)	2/0	(H2+C0)/C
M(4/02H)	#17/07u	41.00	C	55477	38406	.00468
00.	00000	• 00 + 00 •				# # 7 00
4	. 78722	.00643	• 00000	0,099.	.1/132	11000
			10000	74582	00000	• 00 658
1.00	1.5/143		1000	0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		401154
1.50	2.36164		10000.	• / 4500		
			00000	.74435		**\O.
7000	0001-00			74162		.01739
2.50	3.93608		00000	700110		
	4.72329	•02029	00000	.74289	00000.	05020.
2000	1701/0			74217	00000	.02319
3.50	5.51050		00000	\ • \ • \ •		80900
	6.29772		00000	CT 1 4 / *		
00 1				74001	00000.	.03184
2• 00	(19/80/		2000			75750
4.00	9.44658		• 00000	1085/*		
			00000	.73715	00000	.04328
00.7	10170.11			7157		.04897
00.4	12.59544	.04897	• 00000	7/25/		37440
	14041		00000	.73431		
700.	19.01.1			7320	00000	.06028
10.00	15.74430	•06028	00000	7. 70.	•	1

TABLE: 37 SURVEY THE STEAM REFORMING OF INCOLINE AND METHANOL (10/90 BY WT)

VIELD TO CARBON RATIO

PRESSURE =5.0: TEMPERATURE = 600.0F

(H2+C01/C	.03329	.04672	.06828	.09121	.11368	.13578	.15757	•17906	.20028	.24196	.28271	.32260	.36168	. 40002	.43764
))/(5))	.33758	.06077	00000	00000	00000	00000	00000	00000	• 00000	00000	00000	00000	00000	00000	00000
(CH4/C)M	.57086	.70590	.73090	.72516	.71955	.71402	.70857	,70320	.69790	.68748	.67729	.66732	,65755	96449.	•63856
(CO/C) M	\$1000.	•00059	.00030	.00029	.00028	.00028	.00028	.00028	.00028	.00028	.00029	•0005	•00059	.00030	.00030
(H2/C1M	.03314								.19999			.32231	.36139	.39972	.43734
(H20/C)H	•00000	.78722	1.57443	2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F)W	00•	• 50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	2.00	00.9	7.00	8.00	9.00	10.00

TABLE: 38 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE #5.0: TEMPERATURE # 800.0F

TIELD TO CARBON RATIO

(H2+C0)/C	13266	18881	.27944	.36641	.44929	.52876	.60525	70679.	.75046	.88663	1.01489	1.13606	1.25075	1.35943	1.46248
C(S)/C	0	.01606	00000	00000	00000	00000	.00000	.00000	00000	00000	.00000	00000	00000	00000	00000
CH4/C)#	.54976	.69273	.67811	.65636	.63564	.61578	.59665	.57820	.56035	.52631	.49424	.46395	. 43528	. 40811	.38235
M(3/03)	.00279	.00548	.00528	.00520	•00522	.00527	.00533	.00541	.00548	.00563	.00576	.00587	.00598	•00000	.00613
(H2/C)H			.27416	.36121	.44407	.52349	.59992	.67367	.74498	.88100	1.0001	1.13019	1.24477	1.35337	1.45635
(H20/C)H	00000	.78722	1.57443	2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F)#	00•	• 50	1.00	1.50	2 • 00	2.50	3.00	3.50	00.	2.00	00•9	7.00	9 00	9.00	10.00

TABLE: 39 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10790 BY WT)

PRESSURE #5.0: TEMPERATURE #1000.0F

TIELD TO CARBON RATIO

1H2+C0)/C	.37220	.53846	.76198	.96653	1.15275	1.32346	1.48048	1.62507	1.75823	1.99319	2.19029	2.35364	2.48712	2.59460	2.67996
0/(5)/	.36!87	.02184	00000	00000	00000•	00000	00000	• 00000	00000			00000		00000	00000•
CH4/C)#	.47398	. 60243	.55747	.50633	.45978	.41710	,37785	.34170	.30841	.24967	.20039	.15956		.09932	.07798
M(3/03)	.02429	.04670	.04684	66960.	.04745	.04790	.04824	.04842	1 1 0 % O .	.04803	.04708	17240.		.04210	
(H2/C)M	.34792	.49176	.71514	991954	1 - 1 7530	1.27556	1.43224	1.57665	1.70979		2.14320		2.44311	2.55249	2.63988
(H20/C)H	00000	.78722	1.57443	2.36164	3-14886	3.93608	4.72329	5.51050	6.29772	7.A7215	9.44678	11.02101	12.59544	14.16987	15.74430
(H20/F)W	00	0.6	00.1	1.50	2 • 00	2.50	3.00	3.50	3	9 0		7.00			10.00

TABLE: 40 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 SY WT)

PRESSURE =5.0: TEMPERATURE =1200.0F

VIELD TO CARBON RATIO

(H2+C01/C	7000	190701	1.423108	1.62283	1.91551		0019107	2.37998		77166.7	2.64620		1575/17	2.84349	0 0 0	0110117	2.93774		10/5/07	2.94A42	0000	2.97582
3/(5)3	_		20000	00000•	00000			00000			00000			00000•			00000•			00000		00000•
M(D/AHD)	.34915	44070		97246.	.26408	.20187		015277	11516		.08642	.04487	. () ()	•03709	.02194	- (.01353	0.000		. 9005		10100
H(3/03)	.12298	.2300A	10166					87/07•	. 19692	1 1 4	//cp!•	. 17445		94761 •	.13432		11082	. 106na		•04558	70480	
(H2/C)H	.70526	1 • 00100	1. 195.88		6/21/01	1.96825	2.17.70	0.7/114	2 • 33 4 30	2.44042	710013	2.55791	7.40054		2,76978	7.01.007	7481047	2.85099	0 1 0 0	COE/0+7	2.8AB96	
(H20/C)H	00000	.78722	1.57443	2 . 34140		3.14886	3.03608	3	7.72329	5.51050		0.21/12	7.87215		85011	11.02101		14.5.244	14.16007	/0/07	15.74430	
(H20/F)W	•	04.	00•			00.7	2.50		00.5	3.50	1		2•00		9	7.00	9 (00.0	00.6		00.01	

TABLE: 41 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE =5.0; TEMPERATURE =1400.0F

TIELD TO CARBON RATIO

(H20/F)#	(H20/C)H	(H2/C)H	#(5/0)	CH4/CJM	3/(8)/	1H2+CD1/C
00•	00000	1.13366	.37096	.21453	5	7/102 - 1
• 50	.78722	1.65329	.57235	19156	00000	20,000
1.00	1.57443	2.05839		.09929	00000	2.50471
1.50	2.36164	2.29575	•	.05345	00000	2.77805
2.00	3.14886	2.44198	. 42893	.03024	00000	2.87091
2.50	3.93608	2.53766	.38207	.01803	30000	2.91973
3.00	4.72329	2.60414	.34252	.01130	00000	2.94666
3.50	5.51050	2.65282	.30944	.00740	00000	2.94227
4.00	6.29772	2.69003	.28170	.0000	00000	2.97174
5.00	7.87215		.23827	.00255		2.00165
00•9	9.44658		.20612	.00143	00000	2.98616
7.00	11.02101	2.80695	. 18148	.00086	00000	7.98844
8.00	12.59544		.16205	•00055	•	2.98948
9.00	14.16987		14634	.00036		7.0004
10.00	15.74430		.13340	.00025	00000	2.99086

TABLE: 42 SURVEY THE STEAM REFORMING OF INDOLINE AND METHANOL (10/90 BY WT)

PRESSURE #5.0: TEMPERATURE #1600.0F

YIELD TO CARBON RATIO

(H2+C0)/C 2-17917	2.95789	2.97685	2.98401	2.98730	2,98902	2.98999	2.99058	2.99120	2.99149	2.99163	2.99171	2.99177	2,99179
) 50000 •20246	00000	00000	00000	00000	00000	00000	00000	00000	00000	00000	00000	00000	00000
410195 10195	.00649	.00375	96'00'	,00114	.00071	.00047	.00032	.00017	.00010	.0000			•
(CO/C)M •66476	.70890	.61613		* 48656	91044.			.31871			.22558	.20558	.18885
(H2/C)H 1-51441	2.24899	2.36072	2.44015	2.50074	2.54886							2.78618	
(HZO/C)H •00000	1.57443	2.36164	3.14886	3.93608	4.72329	5.51050	6.29772	7.87215	9.44658	11.02101	12.59544	14.16987	15.74430
(H20/F)W	000	1.50	2.00	2.50	3.00	3.50	00.4	5.00	9	7.00	8.00	9.00	10.00

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of methanol relative to steam ref	forming of the mix	s of gasoline contamination ture.								
At the conventional steam i	reforming temperate	ure of 350-400 F soot was								
produced with a 90/10 mixture of	methanol and gaso	line (by weight) A								
parametric study was conducted to and higher steam to carbon ratio	evaluate the effe	ects of higher temperature								
wegine with to tarbon ratio	with rout differed	it catalysts,								

Soot-free operation was obtained with Girdler catalyst T-2107 at an operating temperature of 750% at a steam to (total) carbon ratio of 3.8. Essentially all the gasoline is converted into light gaseous hydrocarbons, primarily methane. A trace of light-yellow oil droplets could be detected in the cooled product gas condensate.

A 100 hour test showed no deterioration of the T-2107 catalyst activity under the above conditions.